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LANTHANIDES AND ACTINIDES

ANNUAL SURVEY COVERING THE YEARS 1984-1986

ROBIN D. ROGERS* and LILLIAN M. ROGERS
Department of Chemistry, Northern Illinois University, DeKalb, IL 60115
(U.S.A.)

INTRODUCTION

This review has been restricted to compounds of the lanthanides and actinides containing M-C bonds as defined by Section 29 of Chemical Abstracts. The prelanthanides La and Y have been included with the lanthanides because of their similar size and charge. Abstracts of papers presented at conferences, dissertations, and patents have been excluded.

Several review articles appeared in the 1984-1986 period. The broadest reviews covered both organolanthanides and organoactinides and include those by Miller[1] covering 1984 (237 references) and 1985[2] (224 references), Cardin and Norton[3] covering M-C sigma bonds in 1982, Karel and Watson[4] the same for 1983 (214 references) and Winter[5] 1984 (180 references). Organolanthanides were reviewed by Schumann[6-8] (303, 225, 35 references, respectively), Klaus[9] (12 references), McCleverty[10] (32 references), Bocharev, et al.[11] (127 references), Shen[12] (40 references) and Evans[13] (12 references). Watson and Parshall[14] reviewed organolanthanides in catalysis (251 references) and Klenze and Kannellakopulous[15] magnetochemical properties (8 references). Uranocene chemistry was reviewed by Streitwieser[16] (24 references) and Sevast'yanov, et al.[17] (45 references). Marks, et al.[18,19] reviewed organoactinide catalysis of C-H bonds (35, 15 references, respectively) as did Folcher[20] (73 references). Gilje and Cramer, et al.[21] reviewed organoactinide chemistry with phosphoylids (30 references). Sokolov, et al.[22] reviewed the reactions of cyclopentadienyl U(IV) compounds with lewis acids and bases (23 references). Mishin, et al.[23] reviewed Np and Pu complexes with monodentate ligands (53 references). In 1985 the NATO Advanced Study Institute monograph appeared detailing the 1984 ASI in Maratea, Italy covering the "Fundamental and Technological Aspects of Organo-f-Element Chemistry."[24]

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LANTHANIDES

Cyclopentadienyl and Cyclopentadienyl-Like Compounds

(i) Monocyclopentadienyl compounds. Few reports of monocyclopentadienyl lanthanide compounds appeared in 1984-86. The compounds $Cp^{*}CeCl_2 \cdot$pyridine ($Cp^{*} = C_5Me_5$), $Li[Cp^{*}CeCl_3] \cdot$2pyridine, and $Li[(C_5Me_4Propyl)CeCl_3] \cdot$2pyridine were prepared via the reactions of $[pyridinium]_2[CeCl_6]$ with MCp^{*} (M = Na, Li), and $Li(C_5Me_4$-Propyl) at room temperature or -78°.[25] The reaction of NaCp and $CeCl_4 \cdot nTHF \cdot xHCl$ in THF at -40°C was reported to produce $CpCeCl_3 \cdot nTHF \cdot HCl$.[26] Characterization was accomplished via elemental analysis, IR, and thermogravimetry.

The crystal structures of $CpYbX_2(THF)_3$ ($Cp = C_5H_5$; X = Cl[27], Br[28]) were reported (Figure 1). Both are isostructural and contain a pseudo-octahedral configuration with trans halides. The oxygen trans to the Cp ligand has a significantly longer Yb-O separation than the remaining two THF ligands.

Two studies of the catalytic nature of non-Cp lanthanides appeared. The kinetics of butadiene polymerization with Cp or indenyl(Ind) neodymium dichloride-alkylaluminates were studied.[29] Also studied was the polymerization of diolefin in the presence of $CpLnCl_2$ catalysts.[30] The activity of various rare earths in catalyzing the stereospecific production of cis-1,4-polybutadine was found to be Nd > Pr > Y > Ce > Gd.

(ii) Triscyclopentadienyl compounds. Thallous cyclopentadienes (TlCpR) in THF or dme have been used to prepare $Cp_3M(THF)$ (M = Ce, Nd, Sm, Gd, Er), Cp_3M (M = Er, Yb), $(CpMe)_3M$ (M = Nd, Sm, Gd), Cp_2Yb, Cp_2Yb(dme) and $(CpMe)_2Yb$-(THF).[31] For Yb it was observed that Cp_3Yb is reduced by Yb^0 to Cp_2Yb and Cp_2Yb can be oxidized to Cp_3Yb by TlCp. Reinvestigation by the same authors of the reaction between Cp_2Hg and activated samarium metal in THF/ether revealed the formation of $Cp_3Sm(THF)$.[32]

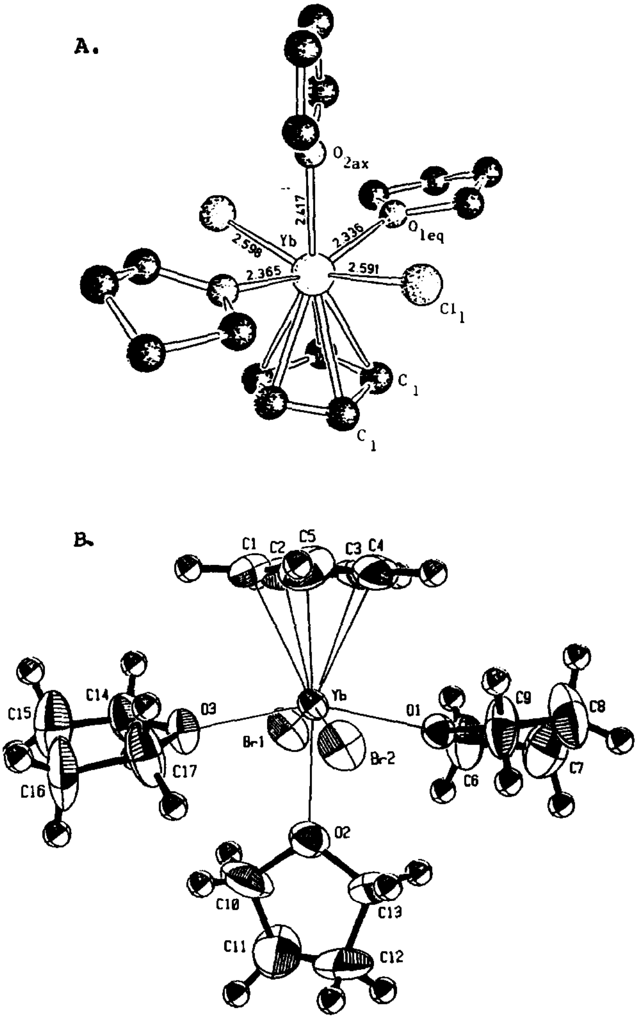

Fig. 1. A) $CpYbCl_2(THF)_3$. B) $CpYbBr_2(THF)_3$. (Reprinted with permission from Journal of Organometallic Chemistry.)

The crystal structures of several triscyclopentadienyl lanthanides appeared: Cp_3La,[33] Cp_3Er,[34] Cp_3Tm,[34] Cp_3Lu,[35] $Cp_3Nd(THF)$,[36] and $Cp_3Lu(THF)$.[37] Three different types of base-free structures were observed. The lanthanum compound forms zigzag chains of $Cp_2La(\mu-\eta^5:\eta^2-Cp)$ units (Figure 2). The La-C distances range from 2.560-3.034Å. The erbium and thulium compounds are isostructural and appear coordinatively saturated with just three η^5-Cp ligands (Figure 3). The Er-C and Tm-C distances range from 2.529(8)-2.824(8) and 2.58(2)-2.83(2)Å, respectively. The closest M···C contacts outside the three η^5-rings are greater than 3.14Å.

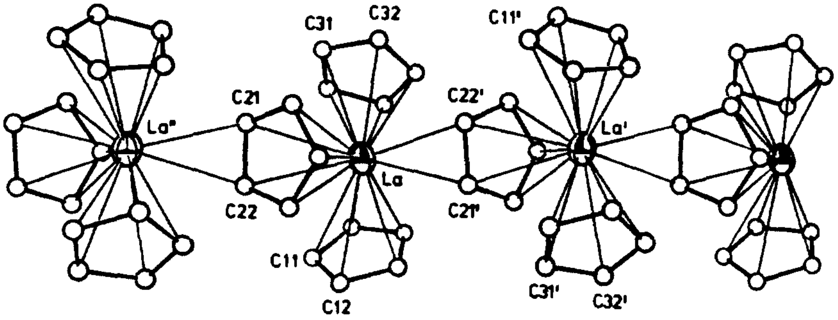

Fig. 2. Cp_3La. (Reprinted with permission from Organometallics. Copyright 1986 American Chemical Society.)

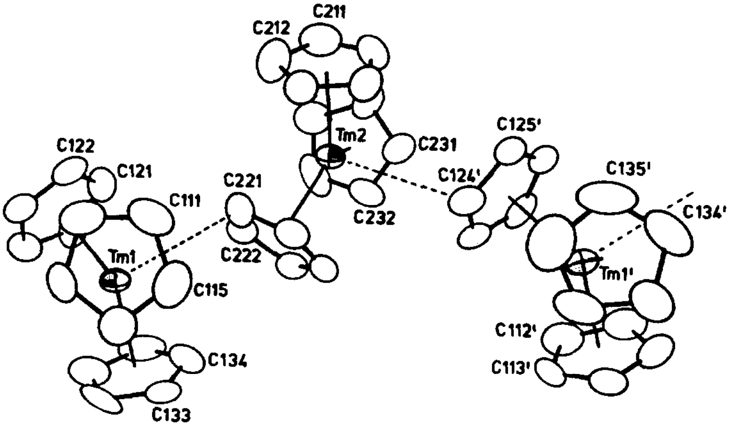

Fig. 3. Cp_3Tm. (Reprinted with permission from Journal of Organometallic Chemistry.)

Triscyclopentadienylutetium (Figure 4) has a coordination member of only 8, and crystallizes as polymeric chains of $Cp_2Lu(\mu\text{-}\eta^1:\eta^1\text{-}Cp)$. The Lu-C distances range from 2.542-2.648Å for the η^5-Cp's and are 2.519 and 2.654Å for the η^1 contacts.

The structures of $Cp_3Nd(THF)$[36] and $Cp_3Lu(THF)$[37] are isostructural with each other and other previously determined members of this series (e.g., $Cp_3M(THF)$ (M = Y,[38] La,[38] Gd[39])). This structure has now been shown to exist over the entire range of the lanthanide elements including Y and La.

The thermal rearrangement of Cp_2Sm(acetate) or Cp_2SmX (X = Cl, Br, I) has been shown to give Cp_3Sm[40]. Samarium acetate and SmX_3 were also obtained in these reversible reactions.

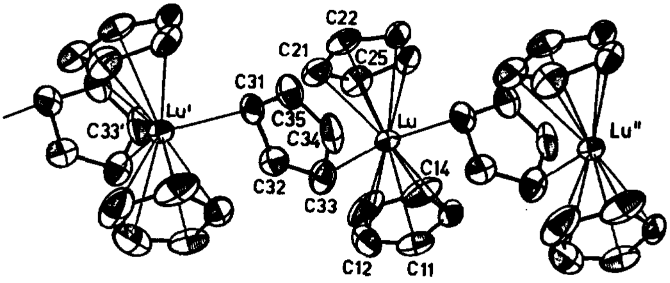

Fig. 4. Cp_3Lu. (Reprinted with permission from Angewandte Chemie International.)

Bond and Deacon[41] have carried out the reversible electrochemical reduction in THF of Cp_3M (M = Sm, Yb, Eu) and $(CpMe)_3Sm$ to give Cp_3M^- species. Thermodynamic stability of the divalent complexes towards oxidation is Eu > Yb > Sm. In the same paper a new synthesis of Cp_3Yb via reaction of $(C_6H_5)_2Yb$ with CpH and $(C_6F_5)_2Hg$ was also reported.

Ligand exchange reactions of $(C_6F_5)_2M$ (M = Yb, Eu, Sm) with CpH, CpMeH, or IndH have produced $Cp_2Yb(dme)$, $Ind_2Yb(THF)_2$, $Cp_2Eu(THF)_n$ (n = 0.5 or 1), $Ind_2Eu(THF)$, Cp_3Sm, $(CpMe)_3Sm$, and $Ind_3Sm(THF)$.[42] Reactions of $(PhCC)_2Yb$ with cyclopentadienes and indenes yielded $Cp_2Yb(dme)$, $(CpMe)_2Yb(dme)$ and $Ind_2Yb(THF)_2$.

Two contributions studied the density, viscosity and surface tension of Cp_3Sm,[43] and the crystal structure of $[Cp_6Nd_2O](C_{12}H_9N_2)_3Cl\cdot mTHF$.[44] In the latter each Nd atom is η^5-bonded to three Cp rings and two Cp_3Nd units bridge via oxygen to form $\{Cp_6Nd_2O\}^{2-}$. The Cp_3Ln compounds appear to be capable of fixation of molecular nitrogen although to a lesser extent than Cp_2Ln complexes.[45]

Xing-Fu, Fischer, and Bombieri prepared the first Cp_3Ln adducts of aliphatic nitrogen.[46] The compounds $Cp_3Ln(NCR)_2$ (Ln = La, Ce, Pr; R = Me or C_2H_5 (La only)) were prepared according to equation 1. Mixtures of 1:1 and 1:2 compounds were observed. The compounds were characterized spectroscopically and crystallographically (Figure 5). The isostructural complexes are trigonal bipyramidally coordinated with each Cp ligand occupying one equatorial site.

$$\begin{tikzcd}
Cp_3Ln(THF) + NCR(xs) \arrow[r, "THF"] & Cp_3Ln(NCR)_2 \\
Cp_3Ln + NCR(xs) \arrow[ur, "50^\circ C", "THF"'] & \\
Cp_3Ln(NCR) + NCR(xs) \arrow[uur, "n\text{-}pentane"'] &
\end{tikzcd} \qquad (1)$$

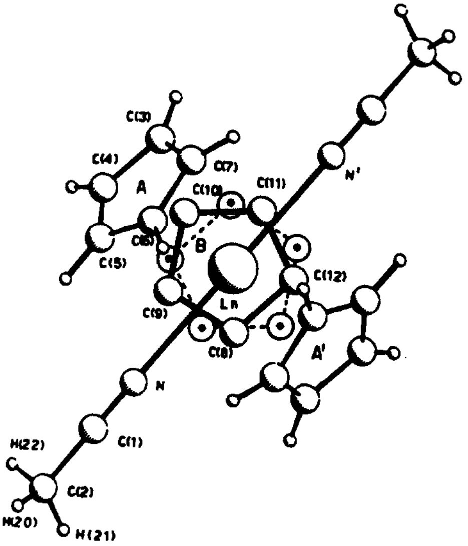

Fig. 5. $Cp_3Ln(NCMe)_2$. (Reprinted with permission from Inorganica Chimica Acta.)

The first bis-isocyanide adduct of a Cp_3Ln complex was prepared and characterized by ^{139}La NMR.[47] This compound, $Cp_3La(CN\text{-}c\text{-}C_6H_{11})_2$, was prepared from Cp_3La and cyclohexylisonitrile in toluene.

Air stable and water soluble complexes of $(C_5(CO_2Me)_5)_3Ln$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb)[48] were prepared by treating $C_5(CO_2Me)_5H$ with the lanthanide carbonates. IR, ^1H NMR and molar conductances are given and suggest some Ln-O coordination.

(iii) Biscyclopentadienyl compounds. Evans[49] reported in 1984 the synthesis and crystal structure of unsolvated, monomeric Cp^*_2Sm (Figure 6). The compound exists as a bent metallocene with a centroid-Sm-centroid angle of 140.1°. The shortest interunit contact is 3.22(1)Å. The compound was a minor product of the metal vapor reaction between samarium and Cp*H. The primary product when worked up in THF was $Cp^*_2Sm(THF)_2$. The unsolvated species could be obtained in good yield by desolvation and sublimation of the major product.

The analogous and isostructural Cp^*_2Eu was also synthesized and structurally characterized.[50] The Eu complex desolvates less readily than its Sm analog and repeated vacuum sublimations are necessary to obtain the base-free compound. A similar bent metallocene structure was proposed for Cp^*_2Yb based on gas electron diffraction studies.[51]

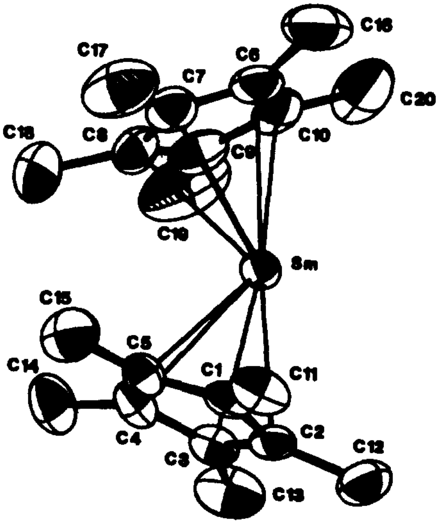

Fig. 6. Cp^*_2Sm. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1984 American Chemical Society.)

Evans and Atwood[52] also reported the characterization and synthetic routes to $[Cp^*_2Sm]_2(\mu\text{-}O)$. This compound (Figure 7) contains linear Sm-O-Sm bridges with the two bent metallocene units twisted 90° relative to each other. It was found to be a common product in reactions of $Cp^*Sm(THF)_2$ with oxygen-containing substrates. The reaction with $OPPh_3$ produced $Cp^*_2Sm(OPPh_3)(THF)$.

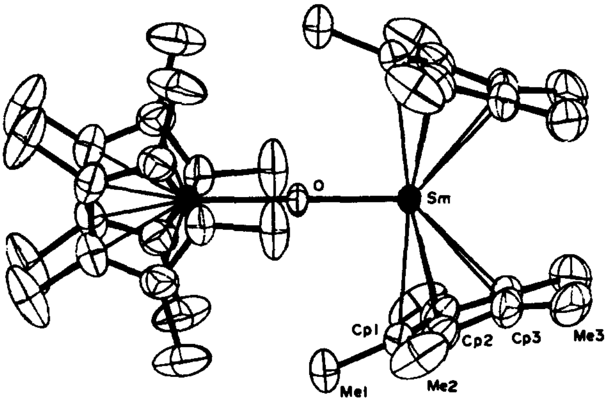

Fig. 7. $[Cp^*_2Sm]_2(\mu\text{-}O)$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1985 American Chemical Society.)

The crystal structures of $[Cp_2GdBr]_2$,[53] $[Cp_2GdBr]_n$,[53] and $[Cp_2YCl]_2$[54] were reported. Both $[Cp_2GdBr]_2$ and $[Cp_2YCl]_2$ exist as discreet dimers, although as reported in the literature, they are not crystallographically isostructural. $[Cp_2GdBr]_n$ is an infinite double chain polymer bridged by halide atoms. Each Gd atom has close contacts to three bromine bridges.

Reactions of anhydrous La, Ce, or $PrCl_3$ with two equivalents of LiCp* in THF followed by crystallization from diethyl ether led to $Cp*_2LnCl_2Li(OEt_2)_2$.[55] The crystal structure (Figure 8) and photoluminescence spectrum of M = Ce was reported.

An asymmetric $Cp*_2Y$ dimer was prepared and structurally characterized (Figure 9).[56] The reaction of YCl_3 and 2KCp* in THF at room temperature led to $Cp*_2YCl_2K(THF)_2$ which when heated lost THF and sublimed as $Cp*_2Y(\mu\text{-}Cl)YClCp*_2$. One Y center is formally seven coordinate, while the other Y is formally eight coordinate containing one terminal chlorine atom. The Y-Cl-Y angle is 162.8(2)°.

Ellis[57] reported the chemiluminescence characteristics of Yb^{3+} species were observed when THF adducts of $Cp*_2Yb$ and $Cp*_2YbCl$ were reacted with O_2 or O_2^-. Shen, et al.[58] reported the synthesis of $[M(THF)_2][L_2LnCl_2]$ (L = Cp*, $CpMe_4Et$, $CpMe_4Pr$; Ln = Nd, Gd, Yb; M = Li, K) by the reaction of $LnCl_3$ with ML in THF. IR and other physical properties were discussed.

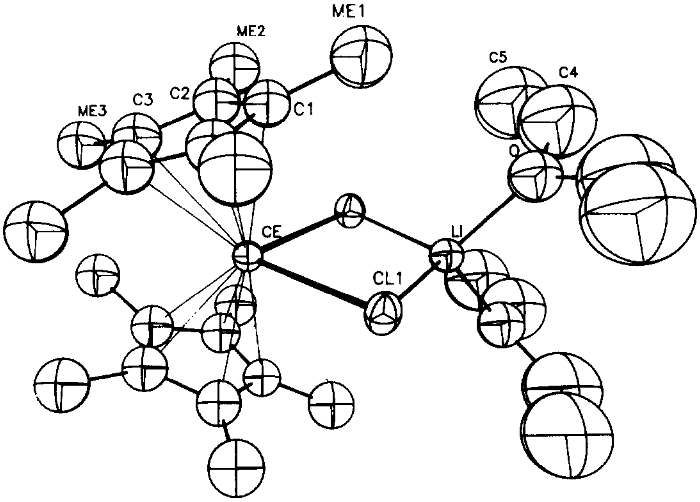

Fig. 8. $Cp*_2CeCl_2Li(OEt_2)_2$. (Reprinted with permission from Organometallics. Copyright 1986 American Chemical Society.)

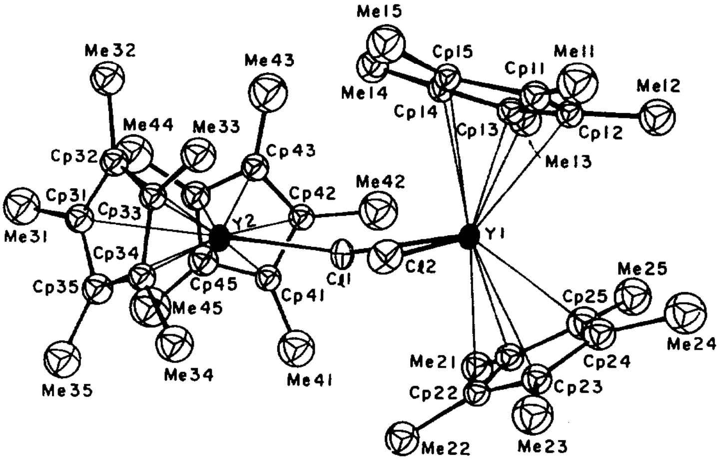

Fig. 9. $Cp^*_2Y(\mu\text{-}Cl)YClCp^*_2$. (Reprinted with permission from Organometallics. Copyright 1985 American Chemical Society.)

(iv) Biscyclopentadienyl adducts and non-halide complexes. Liquid ammonia reactions of Yb^0 and Cp*H led to the formation of $Cp^*_2Yb(NH_3)(THF)$.[59] The crystal structure of this complex was determined (Figure 10). The $Yb\text{-}NH_3$ distance was observed to be 2.55(3)Å.

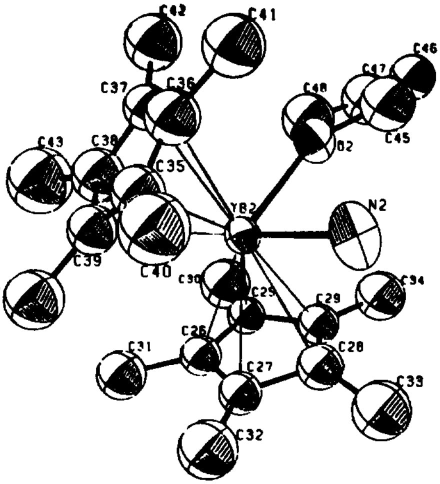

Fig. 10. $Cp^*_2Yb(NH_3)(THF)$. (Reprinted with permission from Organometallics. Copyright 1984 American Chemical Society.)

The reaction of $Cp^*_2Sm(THF)_2$ with $C_6H_5N{=}NC_6H_5$ in toluene yielded $[Cp^*_2Sm](C_6H_5)NN(C_6H_5)[SmCp^*_2]$.[60] The crystal structure of this complex reveals the Sm atoms to be coordinated to the nitrogens in a trans geometry. Also of interest were short phenyl ortho hydrogen to samarium contacts indicative of an agostic interaction. The carbon monoxide insertion product of this complex was also prepared and structurally characterized (Figure 11).[61] The CO's insert into the N-N double bond of azobenzene. Each Sm atom is coordinated to one N and one O of the new ligand.

The 1:1 2,2'-bipyridyl complexes of $[Cp_2LnCl]_2$ (Ln = Gd, Dy, Ho, Er, Yb, Lu) were prepared in THF.[62] Elemental analysis, IR, and X-ray photoelectron spectra were used to demonstrate complexation.

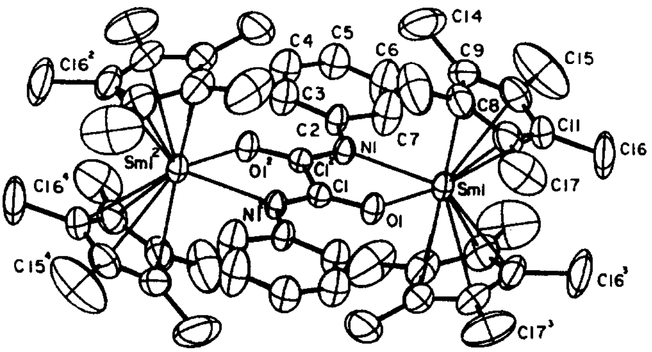

Fig. 11. $[Cp^*_2Sm]_2[\mu,\eta^4\text{-}(C_6H_5N)OCCO(NC_6H_5)]$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1986 American Chemical Society.)

Bis-Cp halide complexes stabilized by THF were again quite common during this reporting period. The synthesis and crystal structures of $Cp^*_2Sm(THF)_2$,[63] $[Cp^*Sm(\mu\text{-}I)(THF)_2]_2$,[63] $Cp^*_2YCl(THF)$,[64] $Cp^*_2SmCl(THF)$,[64] $Cp^*_2SmI(THF)$,[64] and $Cp_2LuCl(THF)$[65,66] were reported. Reaction of SmI_2 in THF with a slight excess of two equivalents of KCp* led to the formation of $Cp^*_2Sm(THF)_2$ (Figure 12), while a 1:1 stoichiometry gave $[Cp^*_2Sm(\mu\text{-}I)(THF)_2]_2$ (Figure 13). The monomeric $Cp^*_2SmI(THF)$ was prepared by oxidation of $Cp^*_2Sm(THF)_2$ with ICH_2CH_2I.[64] Oxidation with ^tBuCl gave $Cp^*_2SmCl(THF)$ while $Cp^*_2YCl(THF)$ was isolated as a by-product of YCl_3 and KCp*.[64] The $Cp^*_2LnX(THF)$ complexes are isostructural (Figure 14). A pseudo-tetrahedral geometry was observed for $Cp_2LuCl(THF)$ although it is not crystallographically isostructural.[65,66]

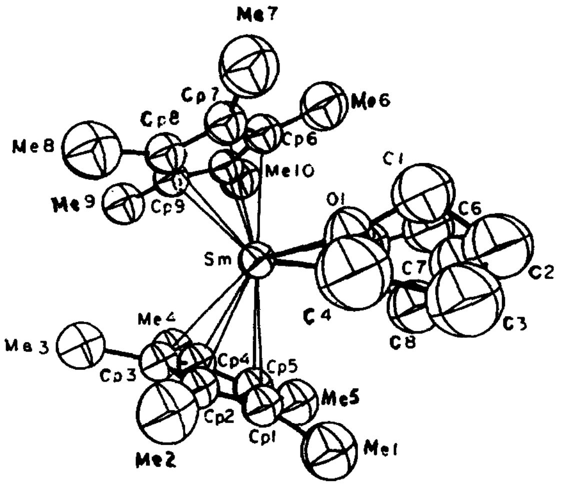

Fig. 12. Cp$^*_2$Sm(THF)$_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1985 American Chemical Society.)

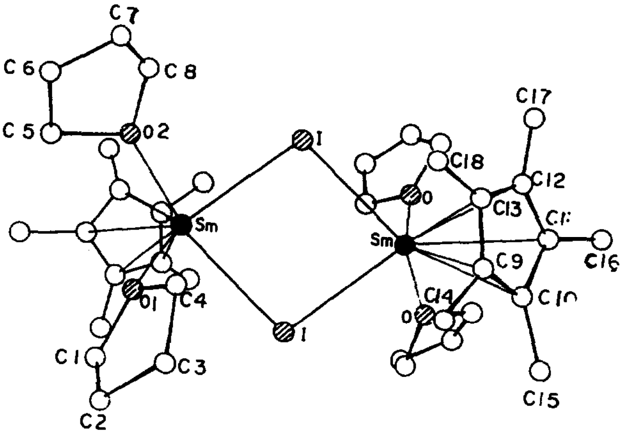

Fig. 13. [Cp*Sm(μ-I)(THF)$_2$]$_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1985 American Chemical Society.)

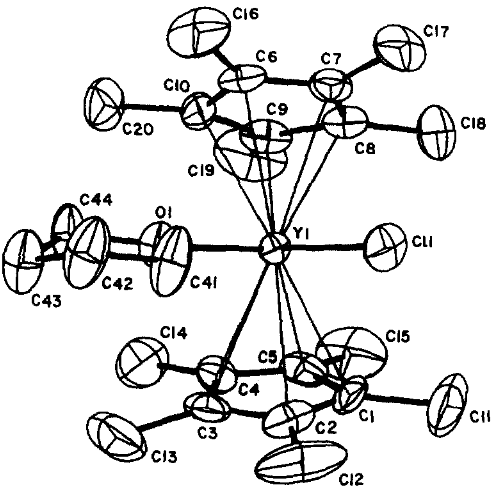

Fig. 14. $Cp*_2YCl(THF)$. (Reprinted with permission from Inorganic Chemistry. Copyright 1986 American Chemical Society.)

The THF adduct, $Cp*_2Sm(THF)_2$, was studied as a CO and CH activating agent. This compound can assemble three CO molecules into a dimetal-substituted ketenecarboxylate: $[Cp*_4Sm_2(O_2CCCO)(THF)]_2$ (Figure 15).[67] When reacted with $C_6H_5C{\equiv}CC_6H_5$, $Cp*_2Sm(THF)_2$ forms $[Cp*_2Sm]_2C_2(C_6H_5)_2$ which further reacts with CO to form $[Cp*_2Sm]_2O_2C_{16}H_{10}$[68] (Figure 16).

Reaction of $Cp_2Yb(MeOCH_2)_2$ and Hg, Tl, Ag, or Cu salts produced $[Cp_2YbX]$ ($X = O_2CMe$, $O_2CC_6F_5$, $O_2CC_5H_4N$, Cl, Br, I, $C{\equiv}CPh$, C_6F_5, $(MeCO)_2CH$, $(PhCO)_2CH$).[69] The crystal structure of $[Cp_2Yb(O_2CC_6F_5)]_2$ was determined and found to be dimeric with each pentafluorobenzoate bridging two metal cations (Figure 17).

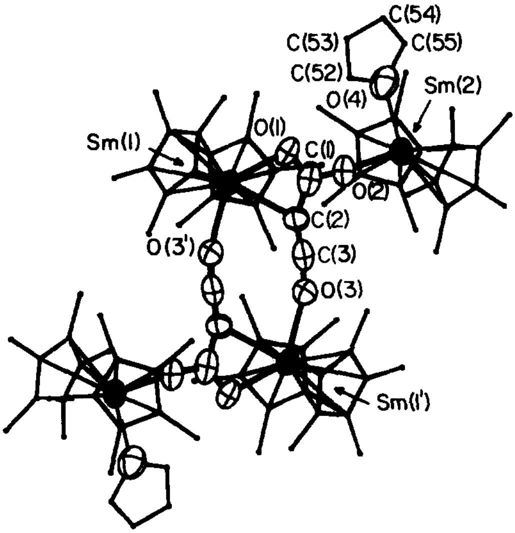

Fig. 15. [$Cp^*_4Sm_2(O_2CCCO)(THF)]_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1985 American Chemical Society.)

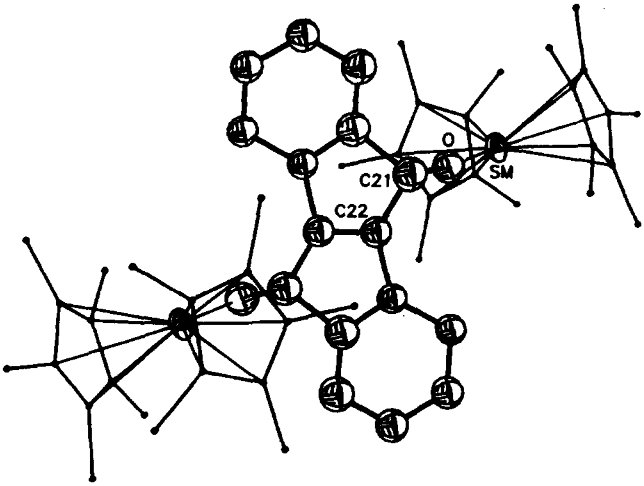

Fig. 16. [$Cp^*_2Sm]_2O_2C_{16}H_{10}$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1986 American Chemical Society.)

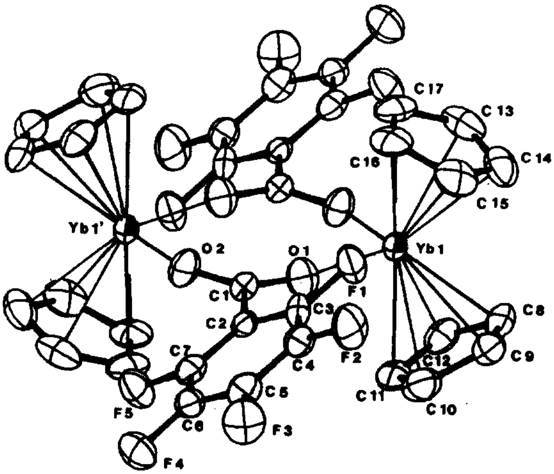

Fig. 17. $[Cp_2Yb(O_2CC_6F_5)]_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

Evans[70] prepared $[(CpR)_2Ln(\mu\text{-}OCH{=}CH_2)]_2$ (R = H, Me; Ln = Lu, Yb, Y) and structurally characterized $[(CpMe)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ (Figure 18). The complexes could be prepared by reaction of $[(CpR)_2LnCl]_2$ with $LiOCH{=}CH_2$ or by thermolysis of $(CpR)_2Y(CH_2SiMe_3)(THF)$ (R = H, Me) or $[Cp_2YbMe]_2$ (in the presence of LiCl and THF).

An aryloxide, $Cp^*{}_2Sm(OC_6HMe_4\text{-}2,3,5,6)$,[71] was prepared by reaction of $Cp^*{}_2Sm(THF)_2$ with 2,3,5,6-tetramethylphenol in toluene and structurally characterized. The Sm-O-C linkage is nearly linear.

In alkoxide chemistry, Evans[72] has reported the reaction of $Cp_2YCl(THF)$ with desolvated KOMe in THF at 30°C leading to dicyclopentadienylyttrium methoxide and a minor reaction product $Cp_5Y_5(\mu\text{-}OMe)_4(\mu_3\text{-}OMe)_4(\mu_5\text{-}O)$. The latter has been characterized crystallographically (Figure 19). This rather interesting structure consists of a square pyramid of yttrium atoms each coordinated to one Cp ligand. Each triangular face contains a triply bridging methoxide ligand and a doubly bridging methoxide group is attached to each base.

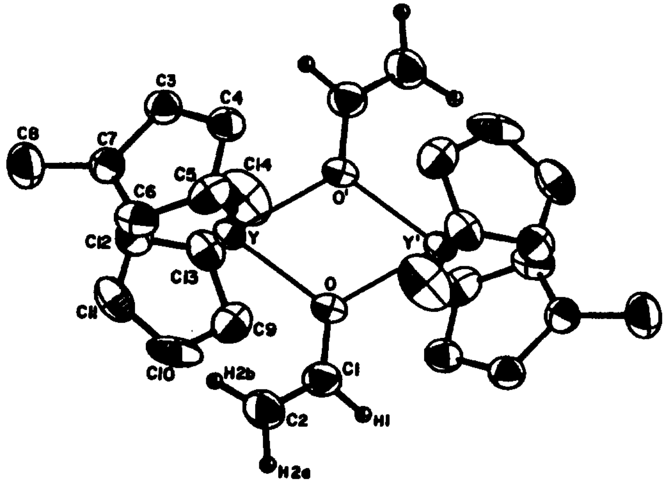

Fig. 18. [(CpMe)$_2$Y(μ-OCH=CH$_2$)]$_2$. (Reprinted with permission from *Organometallics*. Copyright 1986 American Chemical Society.)

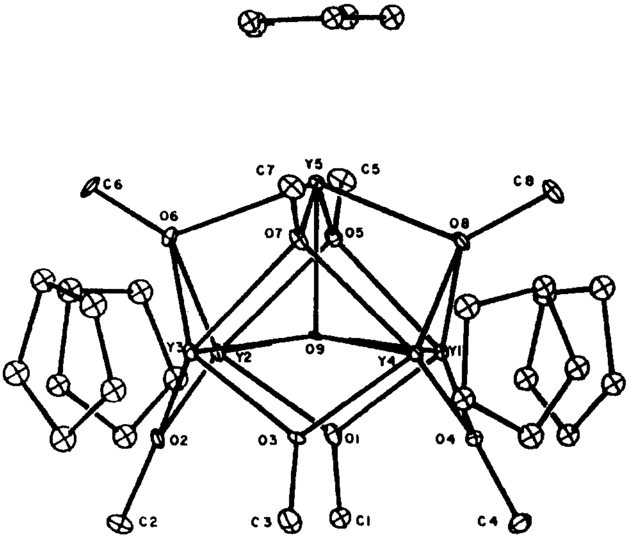

Fig. 19. Cp$_5$Y$_5$(μ-OMe)$_4$(μ_3-OMe)$_4$(μ_5-O). (Reprinted with permission from *Journal of the American Chemical Society*. Copyright 1986 American Chemical Society.)

Synthesis of lanthanide carboxylates were reported by reaction of Cp$_3$Ln or [Cp$_2$LnCl]$_2$ with dicarboxylic acids, carboxylic acids, or their Na salts. The compounds CpYb(OC(O)CHCHC(O)O),[73] CpYb(OC(O)(CH$_2$)$_n$C(O)O) (n = 0-2),[73] CpYb-

$(OC(O)C_6H_4C(O)O)$,[73] Cp_2YbO_2CR (R = CMe_3, CCl_3, Et, CH_2Cl),[74] $(Cp_2YbO_2C)_2R$ (R = CH_2, CH_2CH_2, o-C_6H_4, p-C_6H_4)[75] were reported. In addition, acetates prepared from $[Cp_2LnCl]_2$ and NaOAc in THF were prepared: Cp_2LnOAc (Ln = Sm, Gd, Tb, Dy, Ho, Tm, Lu).[76]

Andersen[77] reported the divalent Yb metallocene, $Cp^*{}_2Yb(OEt_2)$, reacts with $Mn_2(CO)_{10}$ to yield $Cp^*{}_2YbMn(CO)_5\cdot\frac{1}{2}$toluene. This was shown by crystallographic analysis to consist of polymeric sheets of $[Cp^*{}_2Yb(\mu\text{-}OC)_3Mn(CO)_2]$ with dimeric $[Cp^*{}_2Yb(\mu\text{-}OC)_2Mn(CO)_3]$ packed between the sheets. The electron transfer properties of the resulting contact ion pairs were studied. Andersen also reported the structure of $(Cp^*{}_2Yb)_2(\mu_3\text{-}CO)_4Co_3(CpSiMe_3)_2$ (Figure 20) which resulted from the electron transfer reaction of $Cp^*{}_2Yb(OEt_2)$ and $(CpR)Co(CO)_2$ (R = H, Me, $SiMe_3$).[78]

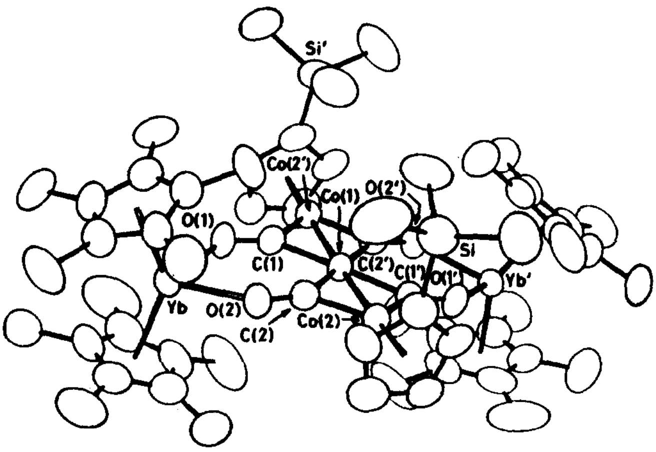

Fig. 20. $(Cp^*{}_2Yb)_2(\mu_3\text{-}CO)_4Co_3(CpSiMe_3)_2$. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

Evans[79] reported $Cp^*{}_2Sm(THF)_2$ and $SmI_2(THF)_x$ react with $Co_2(CO)_8$ to form $Cp^*{}_2(THF)SmCo(CO)_4$ and $[SmI_2(THF)_5][Co(CO)_4]$, respectively. Disproportionation of a similar reaction of $Co_2(CO)_8$ with $[Cp^*SmI(THF)_2]_2$ leads to the same products.

A novel thiolate, $[Cp^*{}_2Lu(\mu\text{-}S\text{-}{}^tBu)_2Li(THF)_2]$[80] was crystallographically characterized (Figure 21). Reaction of $Cp^*{}_2LuMe_2Li(THF)_2$ with two equivalents of ${}^tBuSH$ in OEt_2 gave the thiolate complex. The Lu-S distances are 2.709(3) and 2.723(3)Å. Bis-Cp* alkoxides were also prepared by reaction of $Cp^*{}_2LuMe_2Li(THF)_2$ and ${}^tBuOH$ (yielding $Cp^*{}_2LuO^tBu(THF)$).

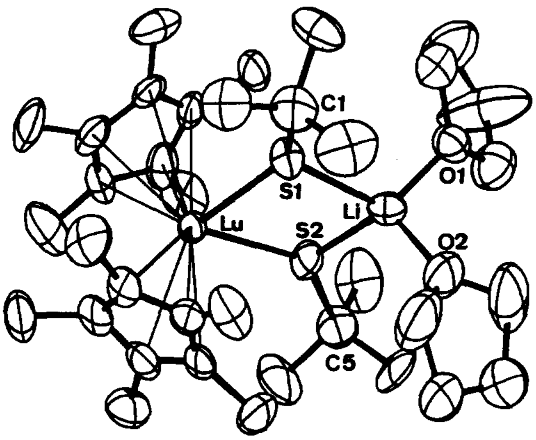

Fig. 21. $[Cp^*_2Lu(\mu\text{-}S\text{-}^tBu)_2Li(THF)_2]$. (Reprinted with permission from Angewandte Chemie International.)

The first structural characterization of an organolanthanoid-phosphane was reported in reference 81 (Figure 22). In $Cp_2Lu(PPh_2)_2Li(tmed)\cdot\frac{1}{2}$toluene the Lu-P separations are 2.782(1) and 2.813(2)Å. The first organolanthanoid-silicon bond was also structurally characterized in reference 82. In $[Li(dme)_3][Cp_2Sm(SiMe_3)_2]$ (Figure 23), the Sm-Si bond lengths are equivalent by symmetry at 2.880(2)Å. Both the Sm compound and its Lu analog were prepared by the reaction of $[Cp_2LnCl]_2$ with $Li(SiMe_3)$ in dme.

Two borohydride complexes were synthesized. The reaction of $[Cp_2YCl]_2$ with $NaBH_4$ in THF gave $Cp_2Y(BH_4)(THF)$[83] in 67% yield and in dme gave $Na[Cp_2Y(BH_4)_2]$[83] in 66% yield.

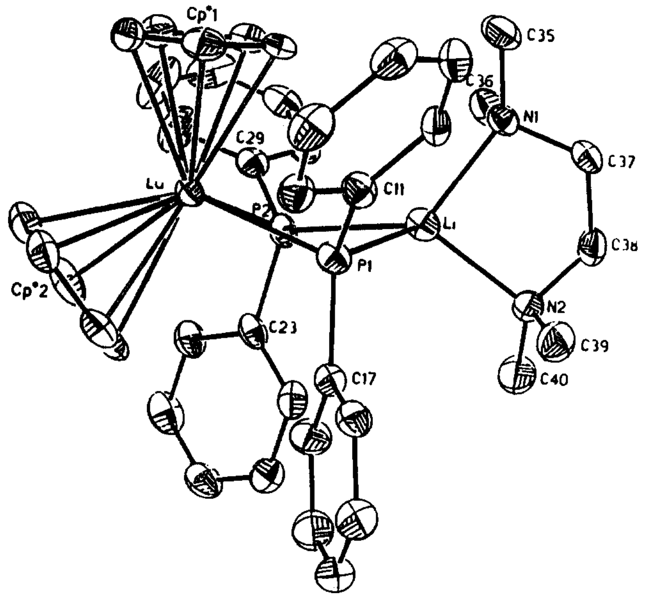

Fig. 22. $Cp_2Lu(PPh_2)_2Li(tmed)\cdot\frac{1}{2}$toluene. (Reprinted with permission from Angewandte Chemie International.)

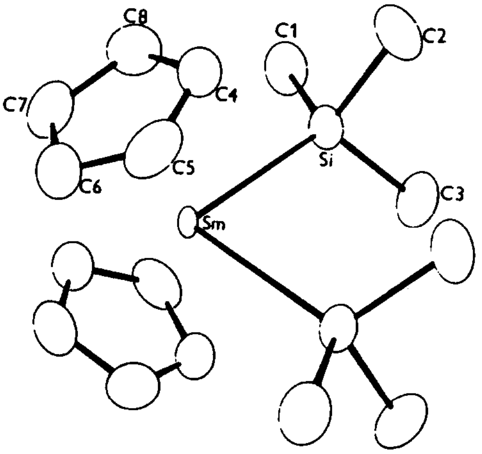

Fig. 23. $[Cp_2Sm(SiMe_3)_2]^-$ anion. (Reprinted with permission from Organometallics. Copyright 1985 American Chemical Society.)

(v) Biscyclopentadienyl hydrides. Ortiz and Hoffmann[84] used MO theory to study the bonding in hydride bridges between Cp_2Ln centers. The preferred orientation for the Cp_2Ln fragments was discussed in relation to several different possible stoichiometries and geometries.

Syntheses and crystallographic characterizations of several of these types of hydride bridges were not lacking. Schumann[85] reported the reaction of alkyl or aryl-Cp_2Lu complexes with H_2 or D_2 to give $[Cp_2LuH]_2$ or $[Cp_2LuD]_2$. Reaction of $Cp_2LuCl(THF)$ with Na in THF gave $[Na(THF)_6][(Cp_2LuH)_3H]$ and Cp_3Lu reacted with NaH or NaD to give $[Na(THF)_6][(Cp_3Lu)_2H]\cdot 2THF$ and its deuterated analog, respectively. The crystal structures of $[Cp_2LuH(THF)]_2$ (Figure 24) and $[Na(THF)_6][(Cp_3Lu)_2H]\cdot 2THF$ (Figure 25) were characterized. The former is dimeric via two hydride bridges, while the latter contains a single linear hydride bridge. Three hydride bridges per metal center were observed in $[Cp_2Y(\mu_3\text{-}H)(\mu_2\text{-}H)AlH_2(THF)]_2$ (Figure 26),[86] $[Cp_2Y(\mu_3\text{-}H)(\mu_2\text{-}H)AlH_2(NEt_3)]_2$ (Figure 27),[87] and $[Cp_2Y]_2(\mu_3\text{-}H)(\mu_2\text{-}H)_2AlH_2(\mu\text{-}H)_2AlH(OEt_2)$ (Figure 28).[87] The latter two compounds were part of a series of hydride complexes prepared which also included $Cp_2YAlH_4(THF)$ and $Cp_2YAlH_4(OEt_2)$.[87]

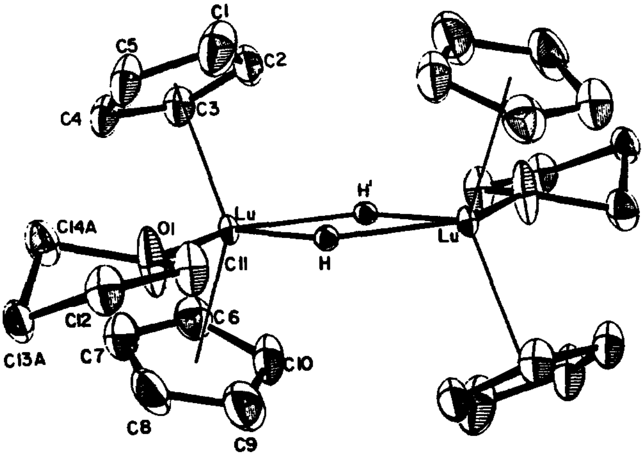

Fig. 24. $[Cp_2LuH(THF)]_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

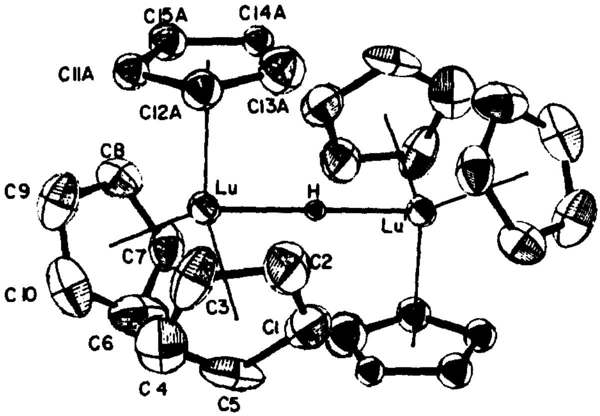

Fig. 25. [Na(THF)$_6$][(Cp$_3$Lu)$_2$H]·2THF. (Reprinted with permission from Journal of Organometallic Chemistry.)

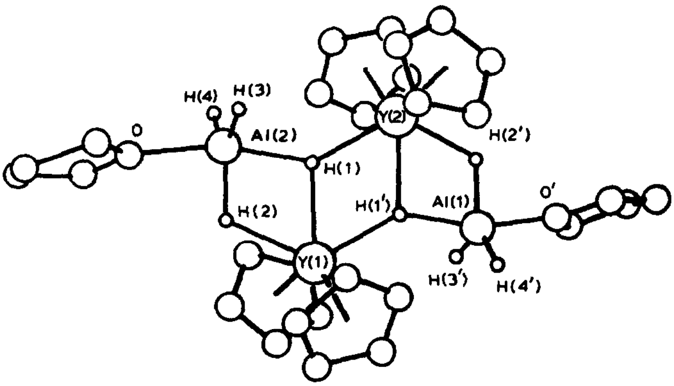

Fig. 26. [Cp$_2$Y(μ_3-H)(μ_2-H)AlH$_2$(THF)]$_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

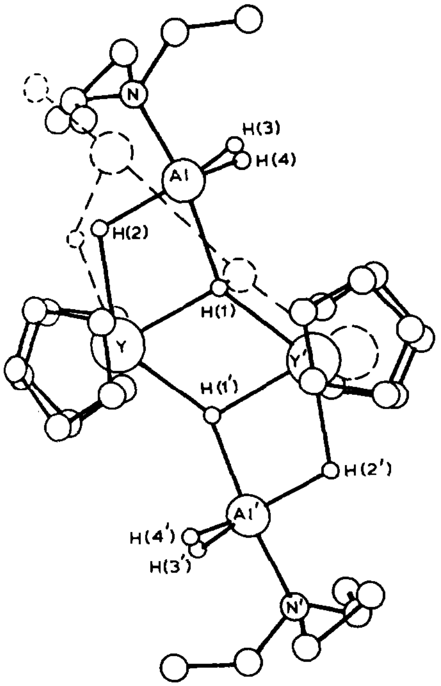

Fig. 27. $[Cp_2Y(\mu_3\text{-}H)(\mu_2\text{-}H)AlH_2(NEt_3)]_2$. (Reprinted with permission from Journal of Organometallic Chemistry.)

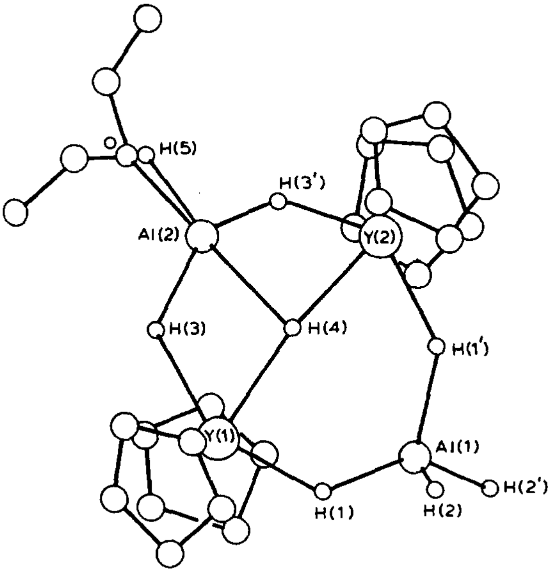

Fig. 28. $[Cp_2Y]_2(\mu_3\text{-}H)(\mu_2\text{-}H)_2AlH_2(\mu\text{-}H)_2AlH(OEt_2)$. (Reprinted with permission from Journal of Organometallic Chemistry.)

Teuben reported a new three-step synthesis of $(Cp^{*}{}_2YH)_n$ starting from $YCl_3(THF)_3$. The synthesis is outlined in equation 2.[88] The hydride product was shown to activate sp^2 and sp^3 C-H bonds.

$$
\begin{array}{ll}
YCl_3(THF)_3 + 2NaCp^{*} \xrightarrow[65^{\circ}C]{THF} Cp^{*}{}_2YCl(THF) + 2NaCl & \\
Cp^{*}{}_2YCl(THF) + LiCH(SiMe_3)_2 \xrightarrow[25^{\circ}C]{OEt_2} Cp^{*}{}_2YCH(SiMe_3)_2 + LiCl + THF & (2) \\
Cp^{*}{}_2YCH(SiMe_3)_2 + \underset{(1\ atm)}{H_2} \xrightarrow[25^{\circ}C]{C_5H_{12}} (Cp^{*}{}_2YH)_n + CH_2(SiMe_3)_2 &
\end{array}
$$

Improved syntheses for trimetallic tetrahydride lanthanide complexes were investigated by Evans.[89] The reaction of $[Cp_2YH(THF)]_2$ with $Li^{t}Bu$ generated the trimer $\{[Cp_2YH]_3H\}\{Li(THF)_4\}$ in 76% yield with by-products $Cp_2Y(^{t}Bu)(THF)$ and $Cp_3Y(THF)$. The perdeutero trimer was formed when $[Cp_2YD(THF)]_2$ was used as the starting material. Similar reactions with LiH and LiMe were described as well as a mechanism for formation of the trimer.

A detailed paper on the reactivity of $[(CpR)_2YH(THF)]_2$ (R = H, Me) with alkenes, alkynes, 1,2-propadiene, nitriles, and pyridine appeared, also by Evans.[90] The starting hydride was prepared by hydrogenolysis of $[Cp_2YMe]_2$ in 10:1 toluene:THF or 10:1 hexane:THF. The new compounds included $[(CpR)_2Y(NCHR')]_2$ (R' = CMe_3; crystal structure), Figure 28, $(CpR)_2Y(CH_2CH_3)(THF)$, $(CpR)_2Y(CH_2CH_2CH_3)(THF)$, $(CpR)_2Y(\eta^3\text{-}CH_2CHCH_2)(THF)$, $[(CpR)_2YC{\equiv}CCMe_3]_2$, $(CpR)_2Y[C(R''){=}CHR''](THF)$ (R" = C_2H_5, C_6H_5), $[(CpR)_2YH(NC_5H_5)]_2$, and $(CpR)_2Y(NC_5H_6)(NC_5H_5)$.

The reactivity of the Sm-H bond with CO was discussed in a paper detailing the formation, isomerization, and crystal structures of cis and *trans*-$[Cp^{*}{}_2Sm(OPPh_3)]_2(\mu\text{-}OCH{=}CHO)$.[91] The structure of the *cis*-isomer is depicted in Figure 29. Both are formed by reaction of $[Cp^{*}{}_2SmH]_2$ with CO in arene solvents and crystallized by adding $OPPh_3$. The *cis*-isomer isomerizes to the *trans*-isomer at room temperature.

The exchange reactions of Cp_3Nd and $Li^{n}Bu$ were studied. The reaction proceeds with the formation of neodymium hydride derivatives.[92]

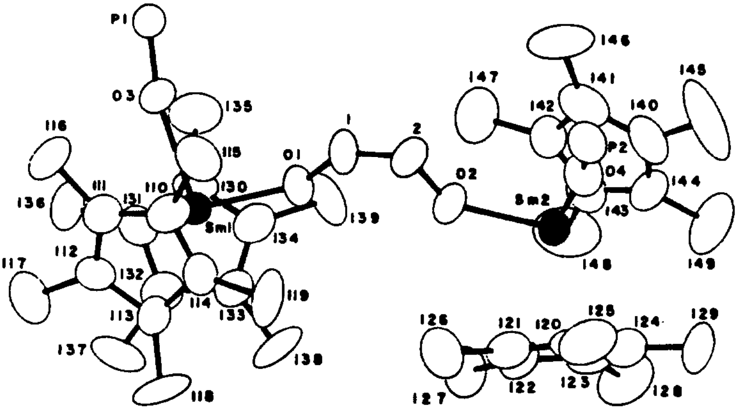

Fig. 29. cis-[$Cp^*_2Sm(OPPh_3)]_2(\mu$-OCH=CHO). (Reprinted with permission from Journal of the American Chemical Society. Copyright 1985 American Chemical Society.)

(vi) Bridged biscyclopentadienyl compounds. Several reports of bridged biscyclopentadienyl lanthanide complexes appeared in the 1984-1986 time period. Three of these by Qian[93-95] discussed the synthesis and thermal decomposition of ($Cp(CH_2)_3Cp)LnR(THF)$ (R = Cl; Ln = Nd, Pr, Gd, Dy, Ho, Er, Lu). Reaction of these with 2,2'-bipyridyl resulted in replacement of the coordinated THF to form 2,2'-bipyridyl complexes. Reactions of the THF adducts with aryllithium or alkyllithium produced several new Ln-C σ-bonded compounds were R = Ph (La, Pr), p-C_6H_4Me (La, Pr), CMe_3 (La, Nd, Y), and CH_2CMe_3 (La).[94,95]

A novel structure appeared containing a $Cp(SiMe_2)Cp^-$ ligand bridging two metal centers instead of chelating one.[96] Reaction of $YbCl_3$ with $Na_2[Cp(SiMe_2)Cp]$ in THF led to this product shown in Figure 30. Other bridged-Cp ligands will be discussed in the next section.

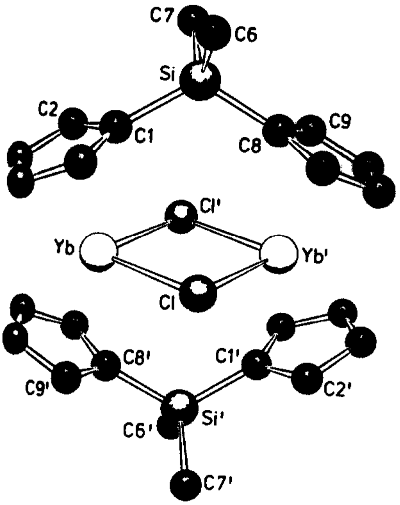

Fig. 30. $[Yb(\mu\text{-}Cl)(\mu\text{-}Me_2SiCp_2)]_2$. (Reprinted with permission from Angewandte Chemie International.)

(vii) Biscyclopentadienyl alkyl, allyl, and aryl compounds. Marks published three papers[97-99] on the synthesis, reactivity, and structures of 4f hydrocarbyl and hydride complexes. In one,[97] the reaction of $Cp^*_2NdCl_2Li(OEt_2)_2$ with $LiCH(SiMe_3)_2$ was reported to yield $Cp^*_2NdCH(SiMe_3)_2$ which further reacted with H_2 to yield $[Cp^*_2NdH]_2$. The latter compound polymerizes ethylene and hydrogenates 1-hexene. The structure of $Cp^*_2NdCH(SiMe_3)_2$ is shown in Figure 31. A possible agostic interaction is noted between Nd and the C2 methyl group. A second contribution[98] broadened the class of compounds $Cp^*_2LnCH(SiMe_3)_2$ to Ln = La, Sm, and Lu in addition to Nd. Activities of the corresponding hydrides were reported to be in the order La $\geq$ Nd >> Lu. The compounds are unreactive toward olefines but Ln = Nd reacts with CO to yield a dimeric dionediolate.

The third major contribution by Marks[99] described the chemistry of similar compounds utilizing bridged Cp backbones: $C_5Me_4(SiMe_2)C_5Me_4$ abbreviated here as $(Cp^*_2SiMe_2)$. Reaction of $LnCl_3$ (Ln = Nd, Sm, Lu) with $Li_2Cp^*_2SiMe_2$ gave the precursors $(Cp^*_2SiMe_2)LnCl_2Li(OEt_2)_2$ and $[(Cp^*_2SiMe_2)LnCl]_2ClLi(THF)_2$. The latter was crystallographically characterized and is depicted in Figure 32. These compounds react with $LiCH(SiMe_3)_2$ to yield $(Cp^*_2SiMe_2)LnCH(SiMe_3)_2$ derivatives. The Ln = Nd complex was structurally characterized (Figure 33). Again, an apparent agostic Nd-H-C interaction is present. Reaction of the hydrocarbyls with H_2 yields the corresponding $[(Cp^*_2SiMe_2)LnH]_2$ dimers. These hydrides polymerize ethylene and oligomerize propylene and 1-hexene.

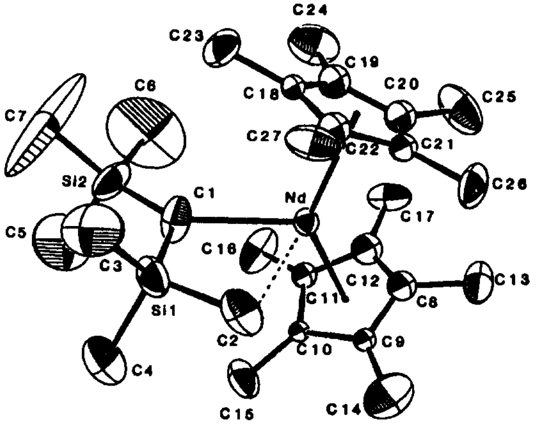

Fig. 31. Cp*$_2$NdCH(SiMe$_3$)$_2$. (Reprinted with permission from Organometallics. Copyright 1985 American Chemical Society.)

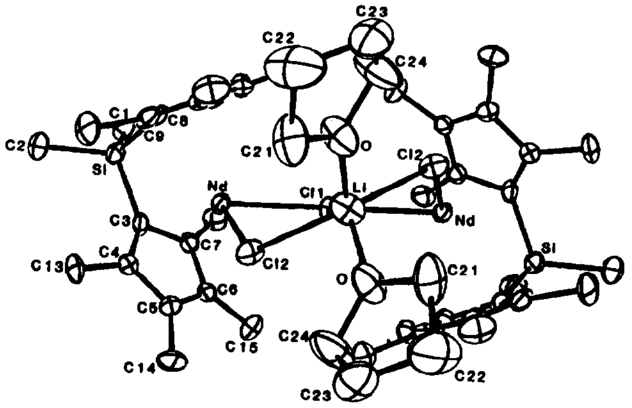

Fig. 32. [(Cp*$_2$SiMe$_2$)LnCl]$_2$ClLi(THF)$_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1985 American Chemical Society.)

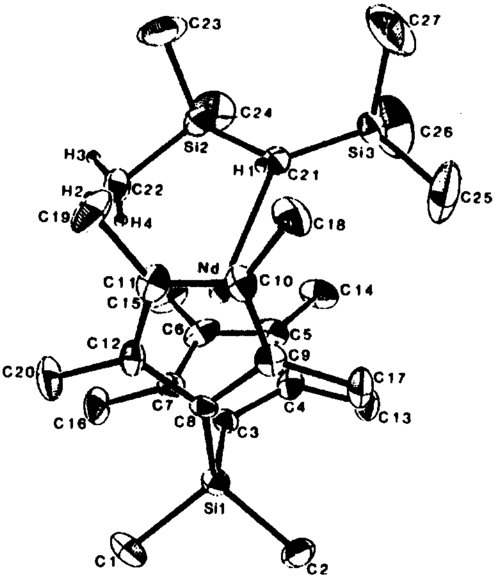

Fig. 33. $(Cp^*_2SiMe_2)NdCH(SiMe_3)_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1985 American Chemical Society.)

Evans[100] reported the crystal structure of $Cp_2YbMe(THF)$ (Figure 34) and its use in isolating $[Cp_2YbH(THF)]_2$ and $[(Cp_2YbH)_3H][Li(THF)_4]$. The Yb-Me distance is 2.36(1)Å. Evans[101] also reported the reaction of $[Cp_2YCl]_2$ with four equivalents of $LiCH_2SiMe_3$ in dme/dioxane which yielded $[Li_2(dme)_2$-(dioxane)]$[Cp_2Y(CH_2SiMe_3)_2]_2$. This complex was structurally characterized (Figure 35) and consists of $Cp_2Y(CH_2SiMe_3)_2^-$ anions and cations consisting of two lithium ions bridged by dioxane and each containing one dme molecule and an interaction with the backside of a Cp ring.

A third Evans contribution,[102] detailed the metal vapor synthesis of $Cp^*_2Sm(THF)_2$ and $(CpMe_4Et)_2Sm(THF)_2$. In addition, $Cp^*_2Sm(THF)_2$ was reported to react with $Hg(C_6H_5)_2$ to form the arene, $Cp^*_2Sm(C_6H_5)(THF)$. Structural characterization (Figure 36) revealed a bent metallocene with a coordinated THF and sigma bonded arene. The Sm-C(phenyl) distance reported was 2.511(8)Å.

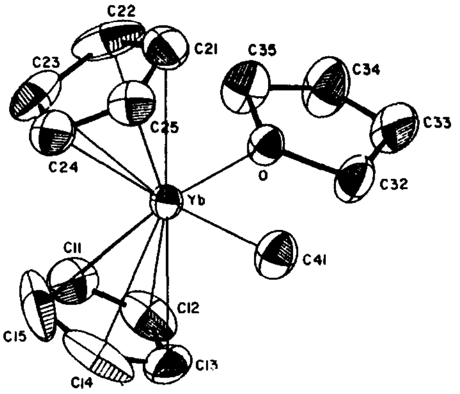

Fig. 34. $Cp_2YbMe(THF)$. (Reprinted with permission from *Organometallics*. Copyright 1986 American Chemical Society.)

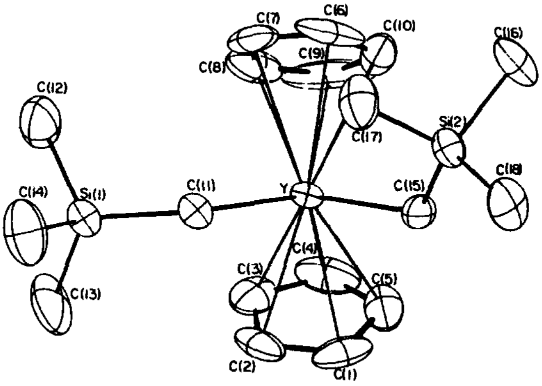

Fig. 35. $Cp_2Y(CH_2SiMe_3)_2^-$ anion. (Reprinted with permission from *Organometallics*. Copyright 1985 American Chemical Society.)

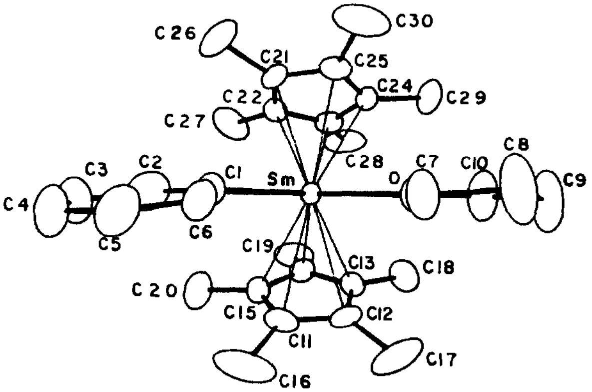

Fig. 36. $Cp^*_2Sm(C_6H_5)(THF)$. (Reprinted with permission from Organometallics. Copyright 1985 American Chemical Society.)

Teuben reported the synthesis and chemistry of $Cp^*_2CeCH(SiMe_3)_2$,[103] $[Cp^*_2CeH]_2$,[103] $Cp^*_2YN(SiMe_3)_2$,[104] and $Cp^*_2YCH(SiMe_3)_2$.[104] The crystal structures of the latter two (Figures 37, 38) reveal short Y-N or Y-C bond lengths and short Y-Me contacts probably indicative of agostic interactions. The amide was prepared from Cp*YCl(THF) and the Na salt while the same reaction with $LiCH(SiMe_3)_2$ led to the hydrocarbyl. Teuben also reported the thermolysis of $[Cp^*_2YH]_2$ in ^{n}octane or benzene to yield $Cp^*_2Y(\mu\text{-}H)Y(CpMe_4CH_2)Cp^*$, a bisyttrium monohydride in which a tetramethylfulvene ligand bridges in a σ-η^5 manner between two yttrium atoms.[105]

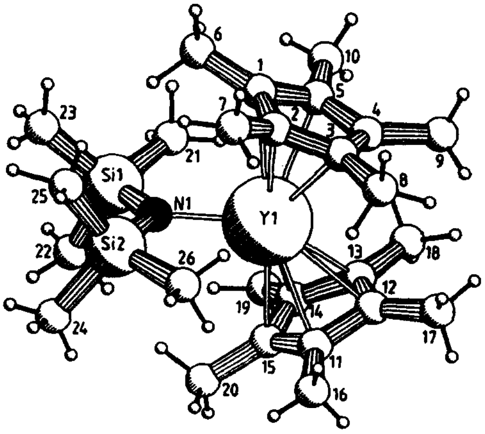

Fig. 37. $Cp^*_2YN(SiMe_3)_2$. (Reprinted with permission from Organometallics. Copyright 1986 American Chemical Society.)

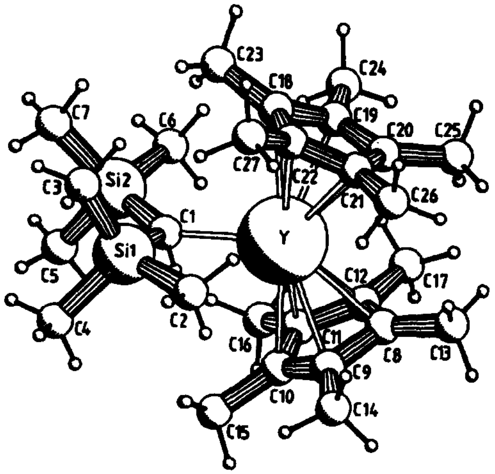

Fig. 38. $Cp^*_2YCH(SiMe_3)_2$. (Reprinted with permission from <u>Organometallics</u>. Copyright 1986 American Chemical Society.)

Schumann had several reports published in this category.[106-117] These included the synthesis and crystallographic characterizations of several new compounds. The reaction of $LnCl_3$ salts with NaCp* or KCp* and LiMe or $LiCH_2SiMe_3$ led to $Cp^*_2Ln(\mu\text{-}CH_3)_2Li(tmed)$ (Ln = La,[106] Pr[107]; Lu[106]), $[Li(dme)_2][Cp^*_2Ln(CH_2SiMe_3)_2]$, (Ln = Lu,[106] Pr[107]), $[Li(tmed)_2][Cp^*LnMe_3]$ (Ln = Yb, Lu),[106,108] and $Cp^*_2Lu(\mu\text{-}Me)_2Li(THF)_2$.[107] Prior to reaction with the lithium reagents, halide derivatives of the complexes $Cp^*_2Ln(\mu\text{-}Cl)_2Na(OEt_2)_2$ (Ln = Pr, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu),[107] $Cp^*_2Ln(\mu\text{-}Cl)_2Na(dme)_2$ (Ln = Pr, Gd, Tb, Dy, Ho, Er, Tm),[107] $Cp^*_2Ln(\mu\text{-}Cl)_2K(dme)_2$ (Ln = La, Ce),[107] $Cp^*_2La(\mu\text{-}Cl)_2K(L_2)$ (L = OEt_2, dme),[108] $Cp^*_2Pr(\mu\text{-}Cl)_2Na(L_2)$ (L = OEt_2, dme),[108] and $Cp^*PrCl_3Na(OEt_2)$[108] were isolated. Reaction of the corresponding trichlorides with NaCp* followed by $LiCMe_3$ in THF led to the formation of $[Li(tmed)_2]$-$[Cp^*Yb(^tBu)_2Cl]$[109] and $[Li(THF)_3][Cp^*Lu(^tBu)_2Cl]$.[109] Use of $Li[(CH_2)_2PMe_2]$ led to the ylide $Cp^*_2Lu[(CH_2)_2PMe_2]$.[110] The crystal structures were determined for $[Li(tmed)_2][Cp^*LuMe_3]$ (Figure 39),[106] $Cp^*_2Pr(\mu\text{-}Cl)_2Na(dme)_2$ (Figure 40),[107,108] and $Cp^*_2Lu[(CH_2)_2PMe_2]$ (Figure 41).[110]

In addition to the permethylated derivatives, Schumann also reported several unsubstituted biscyclopentadienyl complexes. The reaction of $[Cp_2$-$LnCl]_2$ (Ln = Er, Lu) with LiMe in THF and tmed yielded $Cp_2Ln(\mu\text{-}CH_3)_2Li(tmed)$ and in the presence of dme gave $Cp_2Ln(\mu\text{-}CH_3)_2Li(THF)_2$.[111] The Er[111] (Figure 42) and Lu[112] analogs of the tmed adducts were structurally characterized. Triscyclopentadienylneodymium and lutetium were reported to react with Li^{s}Bu and Li^{t}Bu to form Cp_2LnR (Ln = Nd, Lu; R = ^{s}Bu, ^{t}Bu)[113,114] which decomposed to

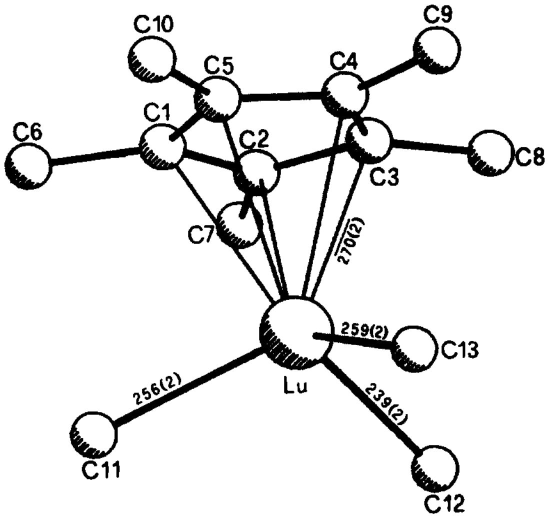

Fig. 39. $[Cp^{*}LuMe_3]^-$ anion. (Reprinted with permission from Journal of Organometallic Chemistry.)

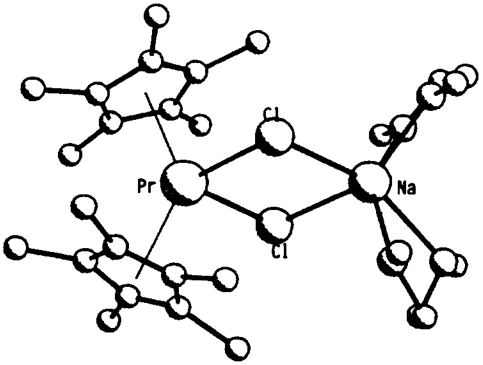

Fig. 40. $Cp^{*}_2Pr(\mu\text{-}Cl)_2Na(dme)_2$. (Reprinted with permission from Inorganica Chimica Acta.)

bis-Cp hydrides. The reaction of $[Cp_2SmCl]_2$ and $[Cp_2LuCl]_2$ with $LiCH(SiMe_3)_2$ formed $Cp_2LnCH_2(SiMe_3)_2$ which further reacted with H_2 to also form bis-Cp hydrides.[113]

Other reactions reported by Schumann included 1) the reaction of $[Cp_2LuCl]_2$ with $LiCH_2PMe_2$ to produce $Cp_2LuCH_2PMe_2$ containing a three-membered Lu-C-P ring,[115] 2) the reaction of $[Cp_2LuCl]_2$ with $Li(CH_2)_2P(^tBu)_2$ to yield a chelate complex,[116] 3) reactions of $Cp_2Lu(^tBu)(THF)$ and $Cp_2Lu(CH_2SiMe_3)(THF)$

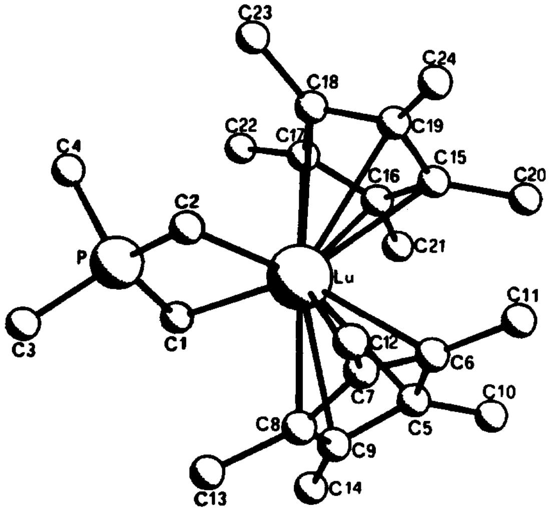

Fig. 41. Cp$^*_2$Lu[(CH$_2$)$_2$PMe$_2$]. (Reprinted with permission from Angewandte Chemie International.)

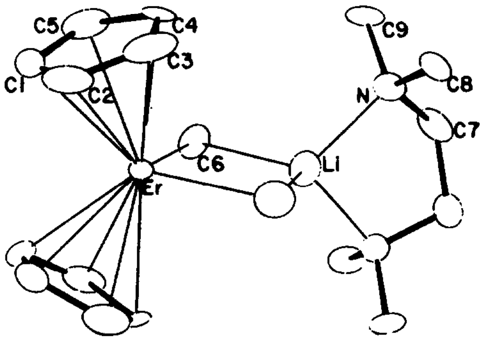

Fig. 42. Cp$_2$Er(μ-CH$_3$)$_2$Li(tmed). (Reprinted with permission from Organometallics. Copyright 1985 American Chemical Society.)

with CH$_2$=PPh$_3$ or Me$_3$SiCH=PMe$_3$ in toluene to produce Cp$_2$LuR methylene triorganophosphoranes,[116] and 4) reactions of Cp$_3$Lu(THF) with CH$_2$=PPh$_3$ to produce Cp$_3$Lu[CH$_2$=PPh$_3$].[117]

Finke and Watson[118] studied atom abstraction oxidative-addition reactions of Cp$^*_2$Yb(OEt$_2$) with alkyl and aryl halides. Detailed mechanisms for the proposed inner sphere "Yb^{III}-Grignard" reactions were given.

Reaction of [Cp$_2$YCl]$_2$ with 2-lithio-N,N-dimethylbenzylamine in OEt$_2$ produced Cp$_2$Y(C$_6$H$_4$-2-CH$_2$NMe$_2$)[119] (Figure 43). Reaction of Cp$^*_2$Ln(OEt$_2$) (Ln = Eu or Yb) with phenylacetylene gave different products for Ln = Eu

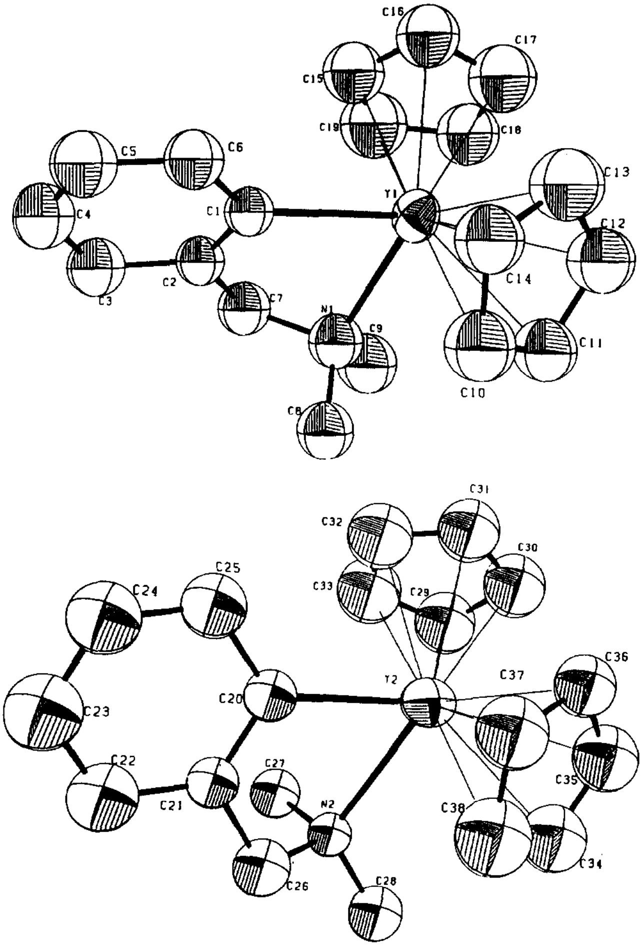

Fig. 43. $Cp_2Y(C_6H_4\text{-}2\text{-}CH_2NMe_2)$. (Reprinted with permission from Journal of Organometallic Chemistry.)

$((Cp^*{}_2Eu_2)(\mu\text{-}C{\equiv}CPh)_2(THF)_4$; Figure 44))^{120} than for Ln = Yb $((Cp^*{}_4Yb_3)(\mu\text{-}C{\equiv}CPh)_4$; (Figure 45))^{120}. Six new 1,10-phenanthroline complexes of Cp_2Ln trifluoroacetates were prepared. ($Cp_2LnOC(O)CF_3(phen)_n$; Ln = Nd, Pr; n = 1 or 2; Ln = Ce, La; n = 2) were synthesized by the reaction of $NaCF_3COO$ with $Cp_2LnCl(phen)_n$.^{121} The complexes were studied by elemental analysis, IR, NMR, and mass spectroscopy. Qian^{122} reported the reactions of $Cp_2LnCl(phen)_n$ with alkynylsodium or alkylithium reagents to produce $Cp_2LnC{\equiv}CPh(phen)$ (Ln = La, Nd), $Cp_2Ln(^tBu)(phen)$ (Ln = La, Nd) and $[Cp(CH_2)_3Cp]NdC{\equiv}CPh(THF)$.

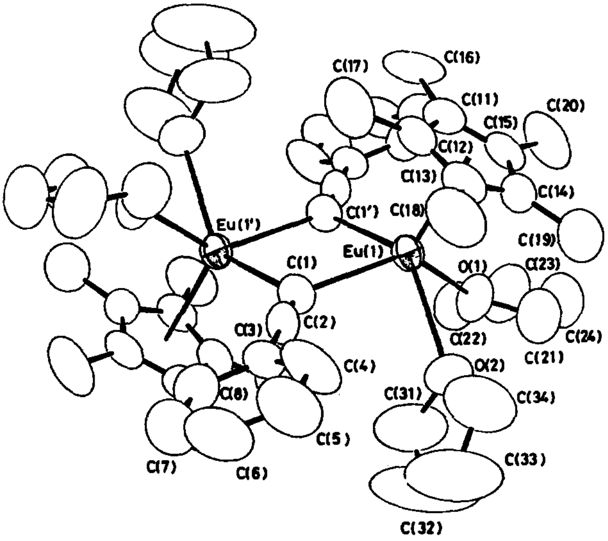

Fig. 44. $(Cp^*_2Eu_2)(\mu\text{-}C{\equiv}CPh)_2(THF)_4$. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

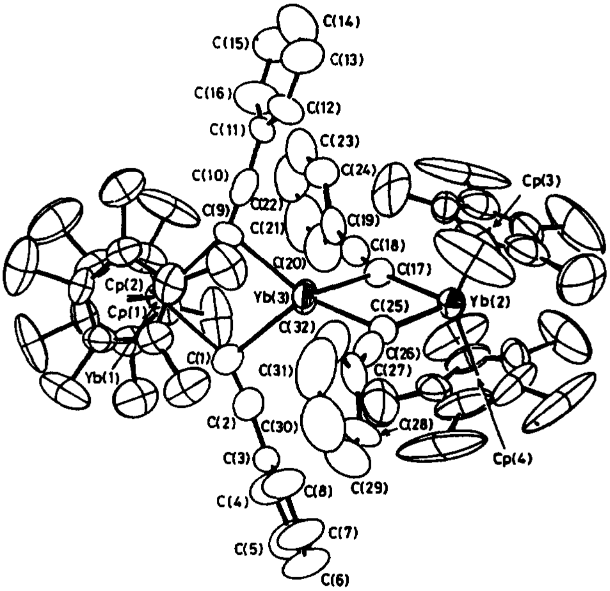

Fig. 45. $(Cp^*_4Yb_3)(\mu\text{-}C{\equiv}CPh)_4$. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

The use of biscyclopentadienyl alkyl compounds was much in evidence during this reporting period. Much of this may be due to the H-H and C-H activation many of these compounds produce. Saillard and Hoffmann presented an extended Hückel MO analysis of this activation in reference 123.

(viii) Indenyl compounds. A few articles on the preparation of indenyl lanthanide compounds appeared. Trisindenyls, $Ind_3Ln(THF)$ (Ln = Ce, Nd, Y) were prepared by reaction of $LnCl_3$ with NaInd in THF and characterized by IR.[124] Bisindenyl chlorides, $Ind_2LnCl(THF)_n$ (Ln = Pr, Nd, Sm, Gd; n = 3,4) were prepared in a similar fashion.[125] (The same paper reported the synthesis of $Cp_2PrCl(THF)_n$ where n = 0, 1, or 2.) Reference 126 utilized the same preparation to prepare indenyl metal chlorides, their hydrochlorides and THF adducts (Ln = Pr, Nd, Sm, Gd) and then utilized the new compounds with aluminum alkyls in polymerization of butadiene. The catalytic activity decreased in the order Nb > Pr > Gd >> Sm. The deuteration and nucleophilic substitution of R_nLnCl_{3-n} (R = heptamethylindenyl; n = 1-3) with $NaNH_2$, MeMgI, LiMe, and NaCp were studied by NMR in reference 127.

(ix) Electronic structure and theory of cyclopentadienyl or cyclopentadienyl-like compounds. The electronic structure and chemical bonding in several organolanthanides were studied with a variety of techniques. These included $[Cp_2YbMe]_2$ (INDO),[128] Cp_4Ce (INDO),[129] Ind_3Sm (INDO),[130] Cp_3Ln (Ln = Pr, Nd, Pm, Sm, Eu, Gd, Tb; EHMO),[131] and $Cp_2LuCl(THF)$ (INDO).[132]

Gas phase He-I and He-II photoelectron spectra were obtained for Cp^*_2Ln (Ln = Sm, Eu, Yb) and ionization energies were calculated from quasi-relativistic Xα-SW calculations.[133] No orbital reason was found for the established non-parallel ring structure.

Photoluminescence studies were carried out for monomeric $(CpMe)_3Tb(THF)$, $(CpMe)_2TbCl(THF)$, and $(CpMe)_2TbMe(THF)$ and for the dimeric $[(CpMe)_2TbCl]_2$ and $[(CpMe)_2TbMe]_2$.[134] Differences in the monomer/dimer spectra and Tb(III) luminescence spectra were developed as useful properties for the study of solvation.

Ellis demonstrated rapid energy transfer between two organolanthanoid complexes in the study of the quenching of the photoluminescence of $Cp^*_2Eu(OEt_2)$ by $Cp^*_2Yb(OEt_2)$.[135] A rate constant of nearly 10^9 $M^{-1}s^1$ was observed.

Parts 8-16[136-144] of the series "The Electronic Structure of Organometallic Complexes of the f-Elements" appeared by Amberger and in part Edelstein. These contributions included very detailed and complete studies of the electronic structures of Cp_3Pr adducts utilizing calculated crystal field splitting patterns and experimental MCD spectra.

Fischer[145] published a study intended to show how details of molecular structure and electronic structure could be obtained from detailed analysis of variable temperature ^1H NMR data on paramagnetic f-element complexes. Evans[146] reported the ^{89}Y NMR spectra of $(CpMe)_3Y(THF)$, $[(CpMe)_2YCl]_2$, $(CpMe)_2YCl(THF)$, $[(CpMe)_2YMe]_2$, $(CpMe)_2YMe(THF)$, $[(CpMe)_2Y(C\equiv CCMe_3)]_2$, $[(CpMe)_2Y(\mu\text{-}H)(THF)]_2$, $\{[Cp_2Y(\mu\text{-}H)]_3(\mu_3\text{-}H)\}\{Li(THF)_4\}$, and $Cp^*{}_2Y(\mu\text{-}Cl)_2K(THF)_2$.

Arene, Aryl, Alkyl, Alkene, and Allyl Compounds not Containing a Cyclopentadienyl Ligand

(i) Arene and aryl compounds. The first structure of a rare earth complex with a neutral π-ligand was determined, $(\eta^6\text{-}C_6Me_6)Sm(\eta^2\text{-}AlCl_4)_3\cdot 1.5$toluene (Figure 46).[147] The Sm-C distances average 2.89(5)Å. Crystals of the complex can be prepared by the reaction of $SmCl_3$, $AlCl_3$ and hexamethylbenzene in refluxing toluene in the presence of Al foil.

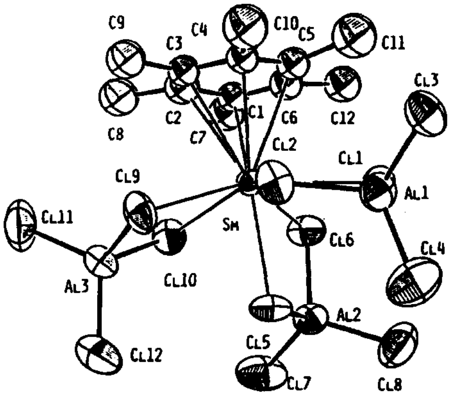

Fig. 46. $(\eta^6\text{-}C_6Me_6)Sm(\eta^2\text{-}AlCl_4)_3\cdot 1.5$toluene. (Reprinted with permission from *Journal of the American Chemical Society*. Copyright 1986 American Chemical Society.)

The remaining aryl lanthanide compounds involve Ln-C sigma bonds to C_6 or C_5 aryl ligands. Two types of complexes containing the chelating [(dimethylamino)methyl]phenyl ligand were prepared and structurally characterized, $Ln[o\text{-}C_6H_4CH_2NMe_2]_3$[148] (Ln = Er, Yb, Lu; Figure 47) and $(\eta^8\text{-}C_8H_8)Ln[o\text{-}C_6H_4CH_2NMe_2](THF)$[149] (Ln = Er, Lu; Figure 48). The homoleptic compound can be prepared by reaction of $LnCl_3$ and $Li[o\text{-}C_6H_4CH_2NMe_2]$ in THF. Similar complexes of Ln = Pr, Nd, Sm, and Tb could not be isolated. If $(\eta^8\text{-}C_8H_8)LuCl(THF)$ is used as the starting lanthanide salt, $(\eta^8\text{-}C_8H_8)Lu[o\text{-}C_6H_4CH_2NMe_2](THF)$ is obtained. Again the procedure failed for the early and middle lanthanides. Reactions of the latter compound with terminal alkynes produced $(\eta^8\text{-}C_8H_8)Lu(C\equiv C^tBu)$ and with the homoleptic Lu compound produced $Lu(C\equiv C^tBu)_3$.

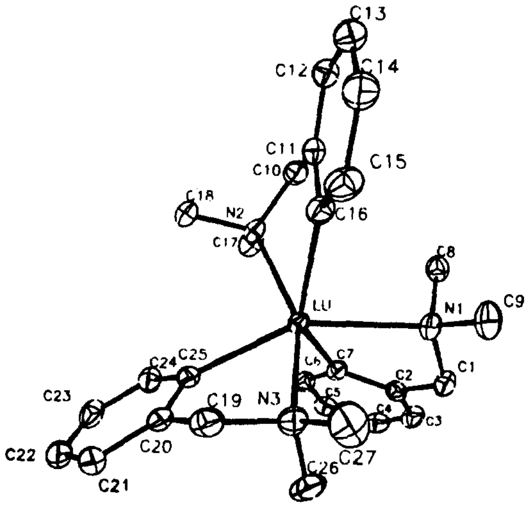

Fig. 47. $Lu[o-C_6H_4CH_2NMe_2]_3$. (Reprinted with permission from Organometallics. Copyright 1984 American Chemical Society.)

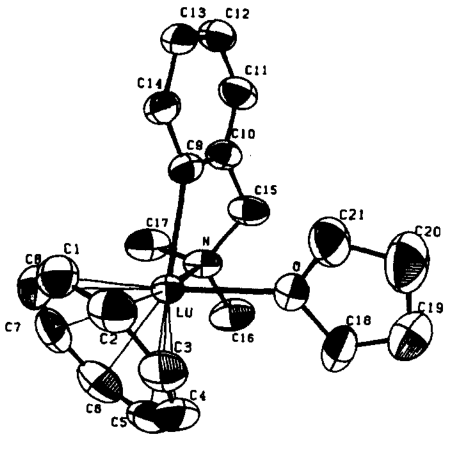

Fig. 48. $(\eta^8\text{-}C_8H_8)Lu[o\text{-}C_6H_4CH_2NMe_2](THF)$. (Reprinted with permission from Organometallics. Copyright 1985 American Chemical Society.)

A few reports of Ln-aryl sigma bonds in π-bonded transition metal aryls appeared. The reaction of bisferrocenyl mercury and Ln^0 (as filings or an amalgam) in THF produced $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]_2Ln(THF)_n$ (Ln = Sm, Eu, Yb; n = 0-1)[150-152] and the reaction of $[Mn(CO)_3(\eta^5\text{-}C_5H_4)]_2Hg$ and Ln^0 filings in THF gave $[Mn(CO)_3(\eta^5\text{-}C_5H_4)]_2Ln(THF)_n$.[150-152] A similar reaction of the Mn reagent with YbI_2 led to the formation of $[Mn(CO)_3(\eta^5\text{-}C_5H_4)]YbI_2(THF)_3$.[153] This approach was extended to $[Cr(CO)_3(\eta^6-C_6H_5)]_2Hg$ and the formation of $[Cr(CO)_3-(\eta^6-C_6H_5)]_2Ln(THF)_n$ (Ln = Sm; n = 2; Ln = Eu; n = 1; Ln = Yb, n = 2).[154-155]

Lanthanide aryl compounds received attention for their reactivity and catalytic activity. The metal vapor synthesis of Ph_3Nd_2 was reported and its activity with $Al_2Et_2Cl_3$ in the polymerization of butadiene studied.[156] Reduction of $LnBr_3$ with sodium napthalide in THF was reported to give finely dispersed highly reactive Ln^0.[157] Several reports appeared on the oxidative addition of aryl halides to the activated lanthanide powders. The preparations of PhLnBr (Ln = Ce, Sm, Eu, Yb)[158,159] and $Ln(\alpha-C_4H_3S)I$ (Ln = Ce, Sm, Eu, Yb),[159] have been reported. Aryl dihalides were utilized in a similar fashion to prepare $Ln(X)(\mu-Ar)Ln(Y)$ (Ln = Yb, Sm; X, Y = Br, Cl; Ar = C_6H_4, $(C_6H_4)_2$, C_4H_2S).[160]

Cerium(0) was activated by a trace of iodine and reacted with alkyl, allyl, and aryl iodides to produce several new organocerium compounds.[161]

Several reactions of the newly produced lanthanide aryl halides were investigated. Transmetallation reactions ($CF_2{=}CFSnBu_3 + PhYbI \xrightarrow{THF\ 20°} PhSnBu_3 + CF_2{=}CFYbI$) and nucleophilic aromatic substitution reactions ($PhYbI + C_6F_6 \xrightarrow{THF\ 30°} C_6F_5Ph + YbIF$)[162] were reported. Spontaneous deoxygenation of the products of the addition of MeYbI or PhYbI to benzoquinone led to the formation of p-xylene (major product 25% yield) for MeYbI and biphenyl (60% yield) for PhYbI.[163] Reaction of excess PhYbI with chalcone produced trans-stilbene, 1,1,3-triphenylpropene and diphenylmethanol.[164] Reaction mechanisms were proposed. The same authors studied several reactions of PhYbI with organic halides in the presence of transition metal catalysts.[165]

Reactions of PhLnI with amines and azoles (R'R"NH) were found to produce R'R"NLnI (Ln = Eu, Sm, Yb).[166] Quantitative yields were observed for imidazole, indole, pyrrole and diphenylamine. An 80-90% yield was observed for aniline and dipropylamine. A brief report on the reactions of RLnX (Ln = Sm, Yb; R = alkyl or aryl; X = halide) with CO appeared.[167] Carbonylation products were observed.

Attempts to study the oxidative-reductive transmetallation reactions of $[(C_6F_5)_3Ge]_2Hg$ with Cp_3Ln (Ln = La, Pr, Yb) produced no reaction.[168] When Cp_2Yb was used $\{[(C_6F_5)_3Ge]_2Hg\}\{Cp_2Yb\}(dme)$ was produced.

The reaction of NaCp with $Eu(PhCOCHCOPh)_2(OAc)$ yielded a sigma bonded aryl, $Eu(C_5H_4)(PhCOCHCOPh)_2$.[169] The structure was confirmed by proton NMR.

(ii) Alkyl compounds. Schumann reported the synthesis of $[Li(dme)]_3-[LuMe_6]$,[170,171] $[Li(tmed)]_3[LnMe_6]$ (Ln = Y, La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu),[171,172] $[Li(tmed)_2][Ln(^tBu)_4]$ (Ln = Tb, Er, Lu),[171,173] $[Li(THF)_4][Ln^tBu_4]$,[171] and $Ln(CH_2SiMe_3)_3(THF)_3$.[171] The reactions were carried out in ether in the presence of the coordinating solvent between $LnCl_3$ and LiR.

The crystal structures of $[Li(dme)]_3[LuMe_6]$ (Figure 49)[170] and $[Li(tmed)]_3[HoMe_6]$ (Figure 50)[172] were carried out. Each exhibits Ln-Me-Li bridging for all methyl groups. Methyl bridges were also observed in the structure of $Yb[N(SiMe_3)_2]_2[AlMe_3]_2$ (Figure 51).[174] There are four Yb-Me-Al interactions and two Yb-Me-Si bridges. Isolation of the compound was accomplished by reaction of $Yb_2[N(SiMe_3)_2]_4$ with two equivalents of Al_2Me_6. In contrast, the crystal structure of $[Li(tmed)_2][Lu^tBu_4]$ (Figure 52)[173] reveals no close cation/anion interactions.

Kauffman, et al.[125] studied the aldehyde selectivity of LnX_2R (Ln = Ce, Pr, Nd, Sm, Gd, Y, La; R = Me, Bu; X = F, Cl, I) prepared in-situ. The prelanthanides exhibited the highest selectivity for heptanal over diethylketone.

Reactions of $Ce(acac)_4$ with excess LiMe led to the isolation of $Li_3[CeMe_6(Li(acac))_3]$.[176] Ethyllanthanoid iodide complexes "EtLnI" were prepared from Ln^0 (Ln = Pr, Nd, Sm) and EtI.[177] The compounds act as catalytic precursors for the condensation of aldehydes.

Various R groups can be added to Yb^{II} via the reaction in THF of PhYbX or MeYbI with RH (R = phenyl-o-carboranyl, phenylethynyl, indenyl, pentafluorophenyl, and 9-fluorenyl).[178] Reaction of $LnCl_3$ (Ln = Nd, Sm, Gd) with MgR (R = butenediyl) in THF gave $LnLCl \cdot MgCl_2(THF)_x$ (x = 0-4).[179] Characterization was accomplished by means of IR, gas chromatography, hydrolysis and thermal analysis. The interactions of LiBu and $LnCl_3$ (Ln = Nd, Ho, Dy, Er) form products that can catalyze the stereospecific polymerization of butadiene.[180] Also studied were the exchange reactions of Cp_3Ln (Ln = Pr, Nd, Gd, Sm) with oligobutadienyllithium.[181]

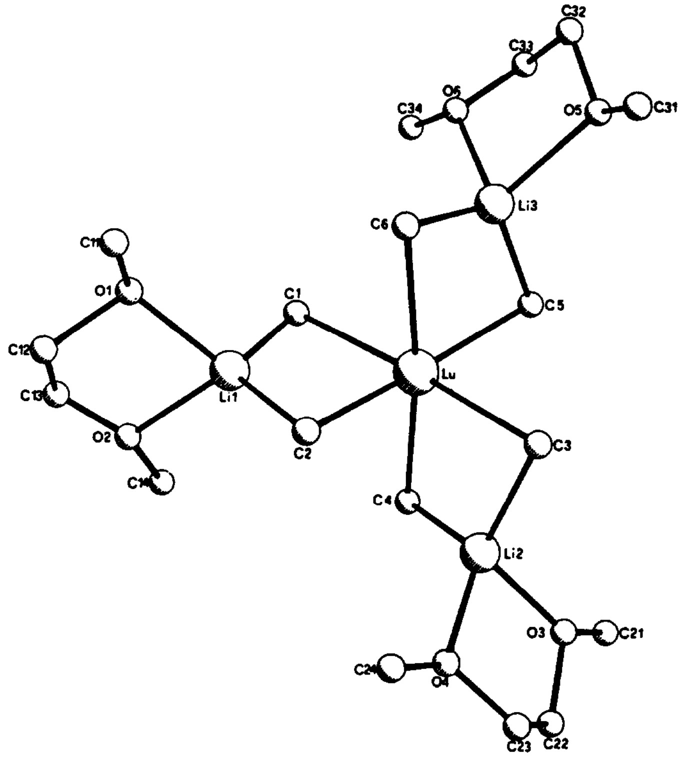

Fig. 49. [Li(dme)]$_3$[LuMe$_6$]. (Reprinted with permission from Journal of Organometallic Chemistry.)

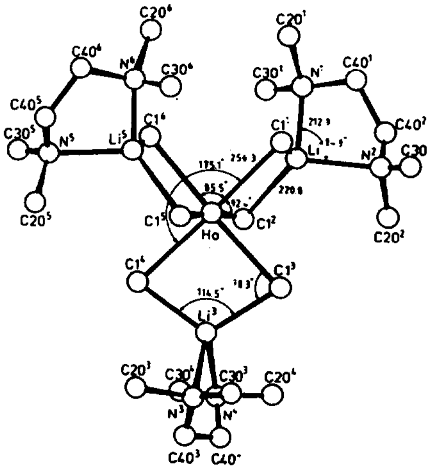

Fig. 50. [Li(tmed)]$_3$[HoMe$_6$]. (Reprinted with permission from Organometallics. Copyright 1984 American Chemical Society.)

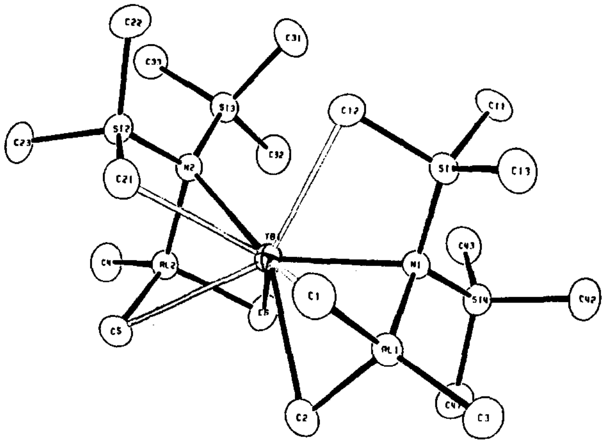

Fig. 51. $Yb[N(SiMe_3)_2]_2[AlMe_3]_2$. (Reprinted with permission from Organometallics. Copyright 1985 American Chemical Society.)

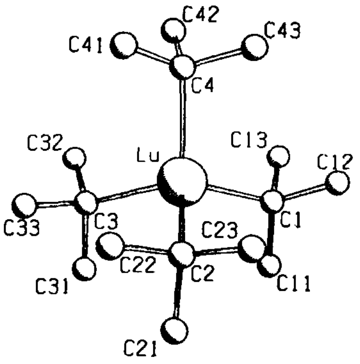

Fig. 52. $[Lu^tBu_4]^-$ anion. (Reprinted with permission from Journal of Organometallic Chemistry.)

The compound $LnCl_2(CPh_3)(THF)_n$ was prepared.[182] The reaction of $ErCl_3$ and $LiCH_2SiMe_3$ in benzene was studied.[183] The alkenyl compound bis(ß-chlorovinyl)ytterbium(II) was prepared by reaction of the organomercury derivative with Yb^0 in THF.[184]

(iii) Allyl compounds. Few fully characterized allyl compounds of the lanthanides appeared. Karsch, Appelt, and Müller published the synthesis and crystal structure of a π-allyl-like diphosphinomethanide complex of La, $La[CH(PPh_2)_2]_3 \cdot$toluene (Figure 53).[185] The structure suggests more ionic character in the bonding. The $La\cdots C$ and $La\cdots P$ distances vary between 2.790(4) and 3.035(1)Å. The bonds to C are slightly shorter than those to P.

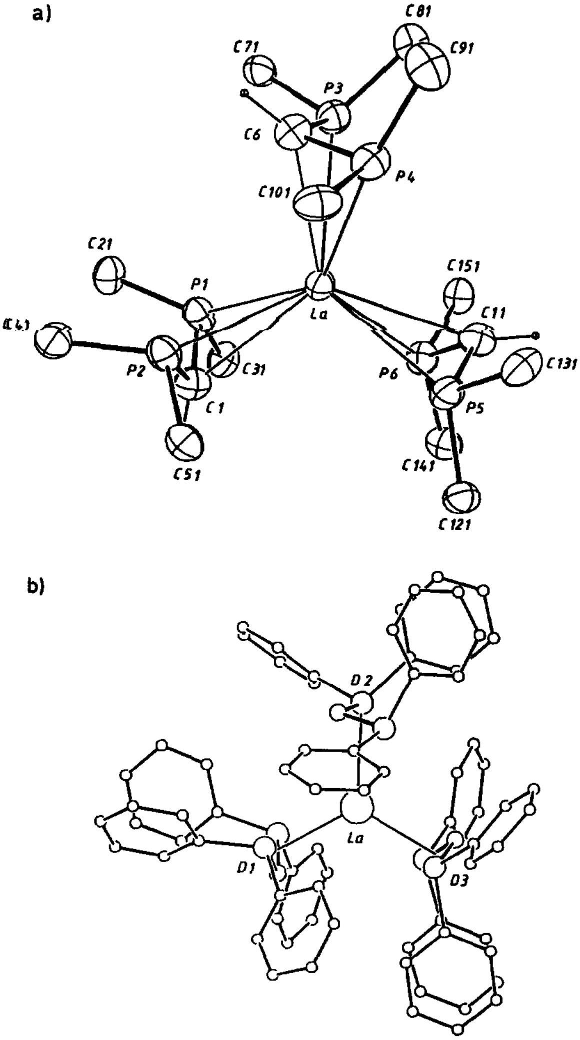

Fig. 53. La[CH(PPh$_2$)$_2$]$_3$·toluene. (Reprinted with permission from Angewandte Chemie International.)

Compounds with the general formula $Li_2Ln(C_3H_5)_5(THF)_n$ (Ln = La, Y; n = 2.5; Ln = Ce, Pr, Nd, Sm; n = 3) were synthesized by the reaction of $LnCl_3$ with

$Li(C_3H_5)$ in THF/OEt_2.[186] Similarly, the compounds $Li_2Ln(C_3H_5)_5(dioxane)_3$ (Ln = Gd, Lu) were prepared when worked up in dioxane.[187]

Miscellaneous

(i) Cyclooctatetraenes. The crystal structures of $[K(C_6H_{14}O_3)]_2[Yb(COT^tBu)_2]$ (Figure 54)[188] and $[K(C_4H_{10}O_2)]_2[Yb(COT)_2]$ (Figure 55)[189] were reported. The compounds were prepared by the reaction of cyclooctatetrane or t-butylcyclooctatetrane with a solution of K and Yb metals in liquid ammonia. Both are sandwich complexes of the Yb^{2+} with K^+ ions interacting with the backside of each COT dianion and the crystallization solvent.

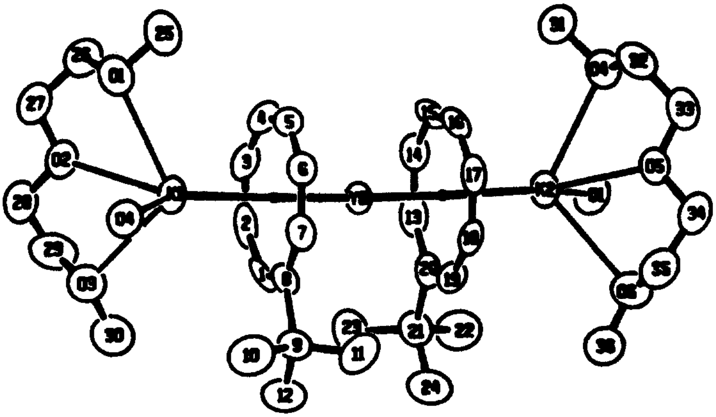

Fig. 54. $[K(C_6H_{14}O_3)]_2[Yb(COT^tBu)_2]$. (Reprinted with permission from Acta Crystallography.)

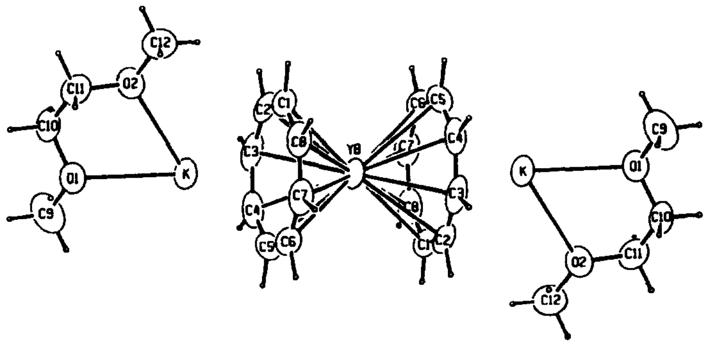

Fig. 55. $[K(C_4H_{10}O_2)]_2[Yb(COT)_2]$. (Reprinted with permission from Organometallics. Copyright 1985 American Chemical Society.)

An SCF-Xα study of cerocene appeared.[190] In addition, the photoelectron spectra and bonding in this compound were studied in reference 191.

(ii) Carbides. Two reports on lanthanide carbides were published in this time period. Burdett discussed the electronic structure of LnB_2C_2 systems (Ln = Y, La, Ce-Lu)[192] and Putyatin, et al. described the synthesis and crystal structures of $Ln_2Ni_5C_2$ (Ln = La, Ce, Pr, Nd, Sm).[193]

(iii) Lanthanide-metal bonds. IR and UV spectroscopy were used to determine that a lanthanide-transition metal bond existed in the new compounds $Ln[M(CO)_mL]_n$ (Ln = Sm, Yb; $M(CO)_mL$ = $Co(CO)_4$, $CpMo(CO)_3$; n = 2, 3).[194] The compounds could be prepared either by reaction of amalgamated lanthanides with $Co_2(CO)_8$ or $[CpMo(CO)_3]_2$ in THF. Treatment of $[(PhCO)_2CH]_2Ln(OAc)$ (Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) with $Na[CpFe(CO)_2]$ gave $[(PhCO)_2CH]_2LnFe(CO)_2LnFe(CO)_2Cp$ reported to contain Ln-Fe bonds.[195] Five new organometallic compounds containing Eu-metal bonds were reported including $Eu(CH(CH_2Ph)_2)_2PPh_2$ and $Eu(CH(CH_2Ph)_2)_2SnPh_3$.[196] The complexes $LnX[M(CO)_mL]$ and $LnX_2[M(CO)_mL]$ where $M(CO)_mL$ = $CpM(CO)_3$ (M = Cr, Mo, W), $M(CO)_5$ (M = Mn, Re), $CpFe(CO)_2$ and X = Cl, Br, I were reported.[197]

(iv) Geometric packing control. Xing-Fu published several reports attempting to define a geometric approach to coordination and organometallic chemistry of the lanthanides and actinides.[198-202] Such factors as the solid angle sum rule, fan angle, coordination vector, gap and hole were studied quantitatively. More than 400 lanthanide and actinide coordination and organometallic structures were studied. The steric angle sum for the organometallic ligands of Ln^{3+} ions in these studies averaged 0.73(10), suggesting such compounds are only stable when their ligand SAS values fall in this region.

ACTINIDES

Cyclopentadienyl and Cyclopentadienyl-Like Compounds

(i) Tetrakiscyclopentadienyl compounds. Bursten and Fang[203] reported $X\alpha$-scattered wave calculations on Cp_4U and Cp_2UCl_2 and observed that the η^5-Cp^- ligand is a better donor to U than Cl^-. Bursten and Fragalà, et al.[204] reported the photoelectron spectra and electronic structures of Cp_4U and Cp_4Th complexes.

A brief report on the oxidation of Cp_4U and Cp_3UCl to uranyl derivatives, cyclopentadiene, cyclopentanone and oxygen-containing oligomers was published by Leonov, et al.[205]

(ii) Triscyclopentadienyl compounds. The absorption and MCD spectra for Cp_3UX_2 ($X = D_2O$, SCN^-, $NCBH_3^-$) compounds were reported by Amberger, Fischer and Yünlü.[206] Hoffman and Tatsumi[207] published an extended Hückel analysis of Cp_3UMe^{2+} and Cp_3UCO^{3+}. They concluded that although no strong π back-donation is expected for an actinide carbonyl interaction there is a good chance of making such compounds.

Nakamura and Tatsumi[208] presented a systematic molecular orbital study of the electronic and geometric structure of Cp_3U complexes. Their observations of strong covalency in U-C(alkyl) σ bonds and weak covalency in the case of U-Cp π bonds are consistent with the observations of Hoffmann and Tatsumi. Partial multiple bond character was indicated in Cp_3U-$CHPR_3$ and Cp_3U-CCR bonds.

The first Th^{3+} crystal structure appeared in 1986, published by Lappert and Atwood, et al.[209] Reduction of Cp''_2ThCl_2 ($Cp'' = C_5H_3(SiMe_3)_2$) with Na/K alloy in toluene gave Cp''_3Th (Figure 56). The compound is monomeric with an average Th-C separation of 2.80(2)Å.

The first example of a U-Sn bond was reported by Casellato, et al.[210] The compound Cp_3USnPh_3 (Figure 57) was prepared from Cp_3UNEt_2 and $HSnPh_3$. The U-Sn distance is 3.166(1)Å.

Andersen, Zalkin, and Brennan[211] published the synthesis and characterization of $[(CpMe)_3U]_2E$ (E = S, Se, Te), and the crystal structures of $[(CpMe)_3U]_2S$ (Figure 58) and $(CpMe)_3UOPPh_3$ (Figure 59). The THF adduct, $(CpMe)_3U(THF)$, reacted with COS, $SPPh_3$, or $Te(^nBu)_3$ to form the bridging chalcogenide complexes. A symmetrical S-bridge was observed in the structurally characterized complex: U-S = 2.60(1)Å, U-S-U = 164.9(5)°. The monomeric complex $(CpMe)_3UOPPh_3$ was isolated when triphenylphosphine oxide was utilized in the same reaction.

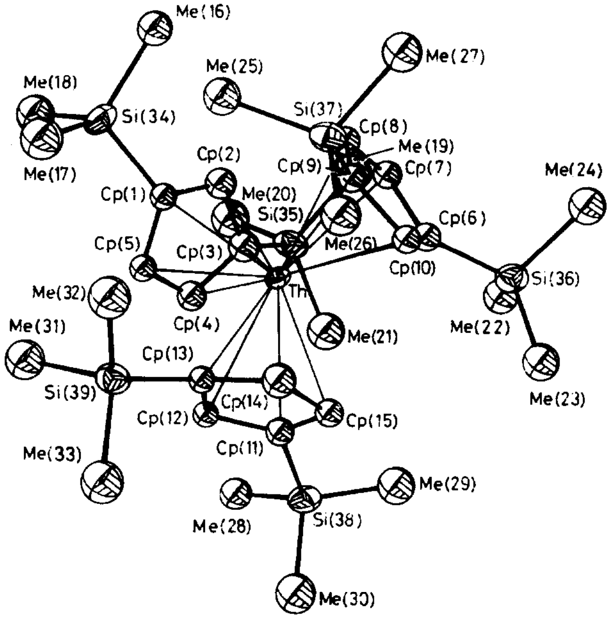

Fig. 56. Cp"$_3$Th. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

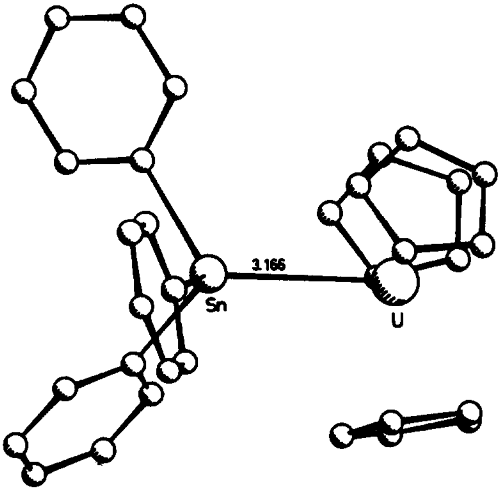

Fig. 57. Cp$_3$USnPh$_3$. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

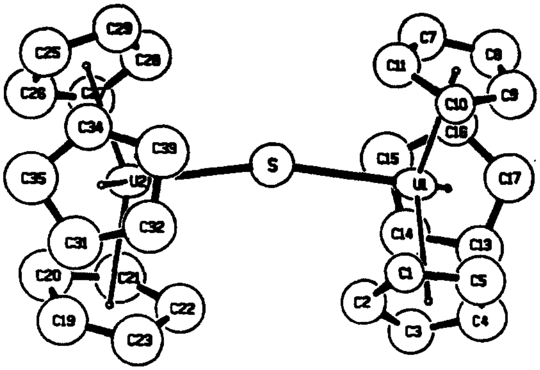

Fig. 58. [$(CpMe)_3U]_2S$. The methyl groups were not located due to severe thermal motion. (Reprinted with permission from Inorganic Chemistry. Copyright 1986 American Chemical Society.)

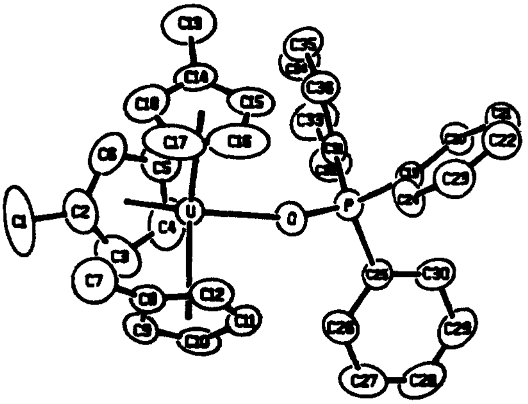

Fig. 59. $(CpMe)_3UOPPh_3$. (Reprinted with permission from Inorganic Chemistry. Copyright 1986 American Chemical Society.)

Zalkin and Brennan[212] also reported the crystal structure of a U^{3+} thioether compound, $(CpMe)_3U(C_4H_8S)$ (Figure 60). The complex was crystallized by adding tetrahydrothiophene to a toluene solution of $(CpMe)_3U(THF)$. The U-S separation is 2.986(5)Å. These same authors published the structure of $(CpMe)_3UPMe_3$[213] (Figure 61). The compound was prepared by the reaction of UCl_3 with NaCpMe in THF and the subsequent addition of PMe_3. The U-phosphine distance is 2.972(6)Å.

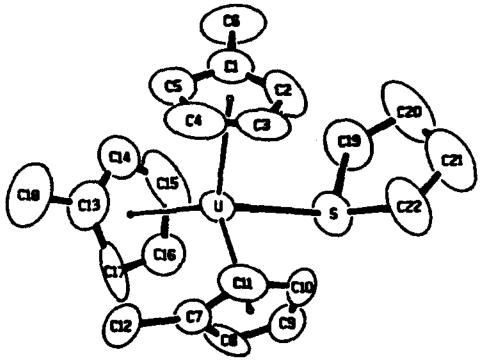

Fig. 60. (CpMe)$_3$U(C$_4$H$_8$S). (Reprinted with permission from Acta Crystallography.)

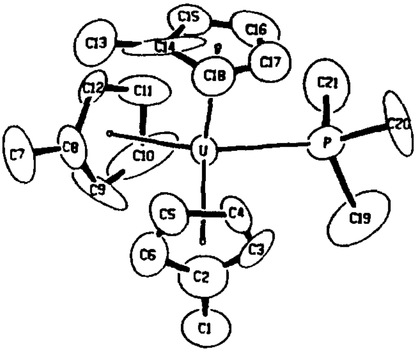

Fig. 61. (CpMe)$_3$UPMe$_3$. (Reprinted with permission from Acta Crystallography.)

The phosphido complex Cp$_3$UPPh$_2$ was prepared by Paolucci, *et al.*^{214} via reaction of Cp$_2$U(NEt$_2$)$_2$ with HPPh$_2$. Mass spectral, IR, VIS and ^{1}H NMR spectroscopic data indicate a free electron pair on P. Two other new compounds, U(NEt$_2$)$_3$PPh$_2$ and CpU(NEt$_2$)$_3$ were also reported.

Reaction of Cp$_3$UCHP(Ph)(R)(Me) with W(CO)$_6$ gave the tungstaenolate (OC)$_5$WC(OUCp$_3$)CHP(Ph)(R)(Me).^{215} The crystal structure of the hemi-toluene solvate of R = Ph is shown in Figure 62. These compounds were reported to isomerize upon heating to Cp$_3$UOCHCHP(Ph)(R)CH$_2$W(CO)$_5$ and the structure of R = Ph was crystallographically established (Figure 63).

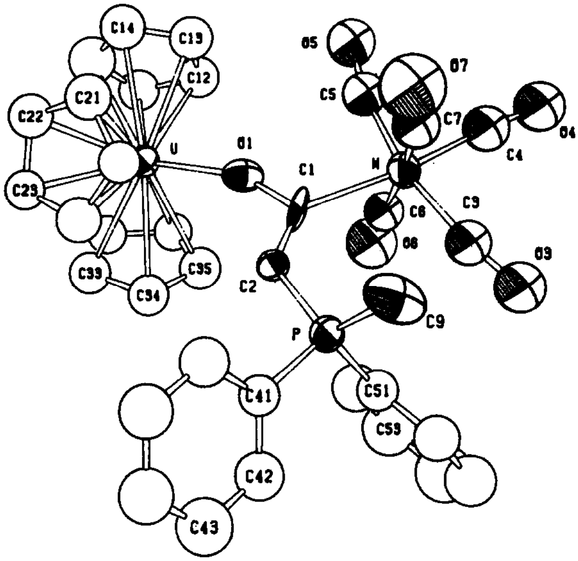

Fig. 62. $(OC)_5WC(OUCp_3)CHPPh_2(Me)$. (Reprinted with permission from Organometallics. Copyright 1986 American Chemical Society.)

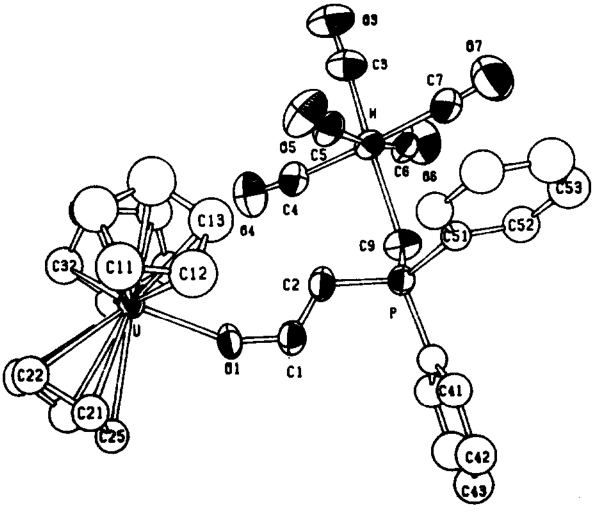

Fig. 63. $Cp_3UOCHCHPPh_2CH_2W(CO)_5$. (Reprinted with permission from Organometallics. Copyright 1986 American Chemical Society.)

Day, Klemperer and Maltbie[216] have prepared and characterized polyoxoanion-supported organoactinides by the reaction of $MW_5O_{19}^{3-}$ (M = Nb, Ta) anions with Cp_3AnCl (An = Th, U). The alkyl ammonium salt, $[N(C_4H_9)_4]_5[Cp_3U(NbW_5O_{19})_2]$, was crystallographically characterized (Figure 64). All four compounds were shown (IR, ^{17}O-NMR) to contain trigonal bipyramidal actinide centers with three η^5-Cp ligands and two axial oxygens from the terminal M-O groups in the polyoxoanion. The An-O bonds were reported to be labile.

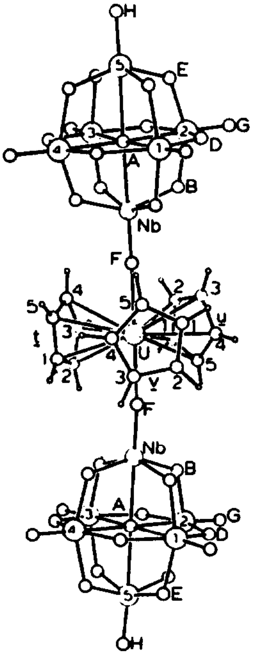

Fig. 64. $[Cp_3U(NbW_5O_{19})_2]^{5-}$ anion. (Reprinted with permission from *Organometallics*. Copyright 1985 American Chemical Society.)

Fischer, *et al.*[217] prepared $[(Cp_3U)_3Co(CN)_6]$ by mixing aqueous solutions of Cp_3UCl and $K_3[Co(CN)_6]$. A polymeric structure similar to $[(Me_3Sn)_3Co(CN)_6]$ (for which an X-ray structure was obtained) was postulated based upon its nonvolability, thermal stability and low solubility. Spectral results also indicated a pseudo-trigonal bipyramidal geometry.

Four bi- and triheteronuclear complexes of uranium and Group 6 metals were prepared and characterized by Dormond and Moise:[218] $Cp_3U[OCM(CO)_2Cp^1]$ (M = Mo, W; Cp^1 = C_5H_5 or C_5Me_5) from Cp_3UCl and Na[M(CO)$_3$Cp^1] or from Cp_3UMe and H[M(CO)$_3$Cp^1]; $Cp_2U[OCMo(CO)_2Cp]_2$ from $Cp_2U(NEt_2)_2$ and H[Mo(CO)$_3$Cp]. All four complexes exhibit low CO stretching frequencies characteristic of isocarbonyl linkages between Mo or W and uranium.

Cramer, Higa and Gilje reported the thermal decomposition of $Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph$ to form $Cp(OC)_2MnC{=}CPMe_2Ph$.[219] The crystal structure of the latter was determined.

Andersen, et al.[220] prepared the first molecular CO complex of uranium, Cp'_3UCO ($Cp' = C_5H_4SiMe_3$). IR stretches of ^{12}CO ν_{CO} = 1976 cm^{-1} and ^{13}CO ν_{CO} = 1935 cm^{-1} were observed. The compound, Cp'_3U, was reported to reversibly absorb CO in solution and in the solid state.

Leonov, et al.[221] reported the reaction of Cp_3U(butyl) with carbon dioxide.

Paolucci, et al.[222] studied the insertion of CO into U-C and U-N bonds in tris-Cp complexes. The compounds Cp_3UX (X = Me, Et, ^{i}Pr, ^{n}Bu, ^{t}Bu, Et_2, PPh_2, $NCBH_3$) were reported to react in solution with CO at room temperature. Spectroscopic measurements agree with a dihapto-acyl or dihapto-carbamoyl formation.

Cramer, Higa and Gilje[223] published an account of the addition of coordinated CO across a uranium-carbon double bond. Reaction of $Cp_3U{=}CHPMe_2Ph$ with $CpMn(CO)_3$ in THF for 3 days at room temperature produced $Cp(OC)_2MnC(OUCp_3){-}CHPMe_2Ph$ (Figure 65). The U-O bond is short at 2.13(1)Å and the U-O-C angle is large at 160(1)°.

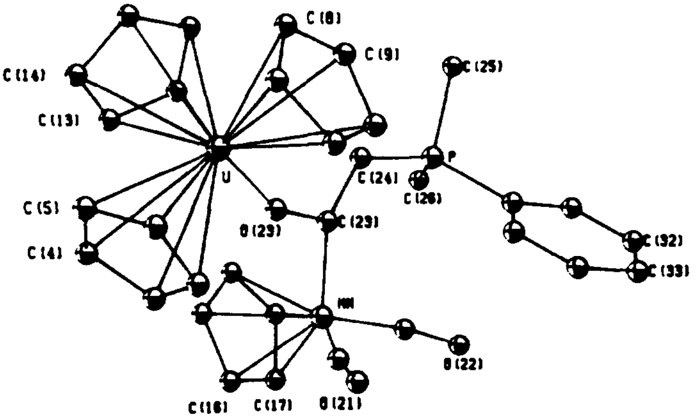

Fig. 65. $Cp(OC)_2MnC(OUCp_3){-}CHPMe_2Ph$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1984 American Chemical Society.)

Karova, et al.[224] reported the isolation of the insertion product $Cp_3U(CO_2CH_2CHCH_2)$ from the reaction of Cp_3U(allyl) with CO_2. Chang and Sung-Yu[225] isolated $Cp_3UCl(COMe)$ as an intermediate in the oxidative addition of Cp_3U with acetylchloride at 6°C. The compound was characterized by ^1H NMR, electrochemical data and its chemical properties.

Reaction of Cp_3UMe with CNC_6H_{11} gave the η^2-insertion product, $Cp_3U[\eta^2\text{-}CMeN(C_6H_{11})]$ according to Zanella, et al.[226] The crystal structure was reported (Figure 66). The bonding parameters, U-N = 2.40(2)Å, U-C = 2.36(2)Å, C-N = 1.25(2)Å, and planarity of the UCCNC fragment are consistent with a C-N double bond.

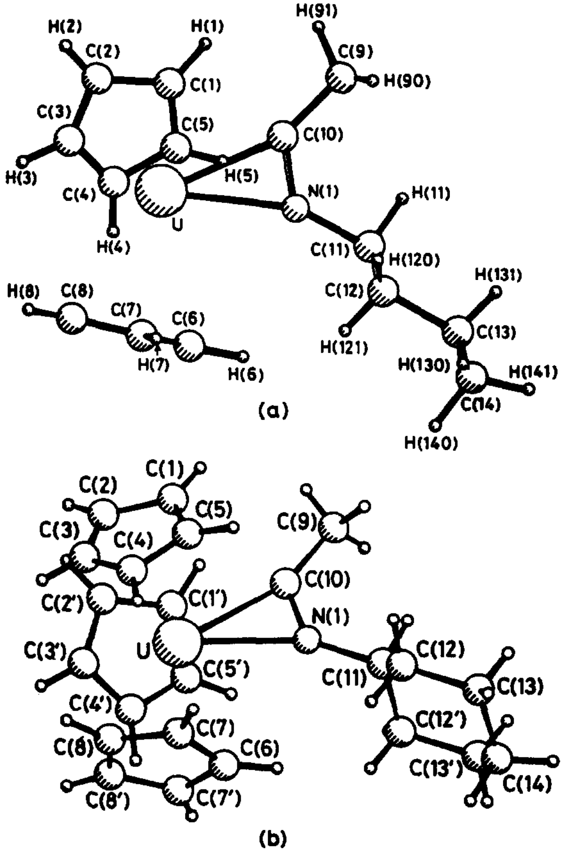

Fig. 66. $Cp_3U[\eta^2\text{-}CMeN(C_6H_{11})]$. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

Paolucci, et al.[227] reported the fragmentation patterns of Cp_3UX (X = NEt_2, η^2-CMe=N(C_6H_{11}), and η^2-CMe=N^nBu) compounds under electron impact. Hydrides of Cp_xU were observed.

Fischer and Aslan[228] prepared the salts, $[Cp_3U(CNR)_2][BPh_4]$ and $[Cp_3U(NCR)(CNR')][BPh_4]$ (R = Me, ^nPr, $^cC_6H_{11}$) by reaction of the BPh_4^- salts of $[Cp_3U(OH_2)^n]^+$ and $[Cp_2(CpMe)U(NCR)_2]^+$ with alkyl isocyanides.

Cramer, et al.[229] prepared $Cp_3U(\eta^2\text{-}CN(C_6H_{11})CHPMePh_2$ by the insertion of CNC_6H_{11} into the uranium-carbon double bond in $Cp_3U{=}CHPMePh_2$. The crystal structure of this compound (Figure 67) revealed U-N = 2.31(2)Å, U-C = 2.44(3)Å, and C-N = 1.39(4)Å. The bonding here suggests multiple bond character in the U-N bond.

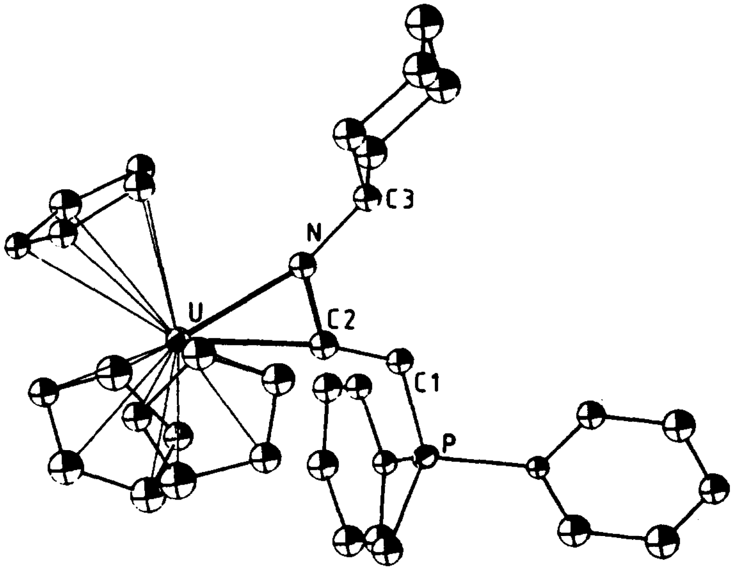

Fig. 67. $Cp_3U(\eta^2\text{-}CN(C_6H_{11})CHPMePh_2$. (Reprinted with permission from Angewandte Chemie International.)

Dormond, et al.[230] reported the formation of iminoalkyl insertion compounds in the reactions of isocyanides with Cp_3UR and $Cp^*{}_2URCl$ (R = alkyl). Reaction with $Cp^*{}_2UR_2$ produced insertion into only one of the U-C bonds. Spectroscopic evidence pointed toward an η^2-structure with strong U-N bonding. Cp_3UMe did not react; however Cp_3U^nBu reacted at low temperature to yield $Cp_3U[\eta^2\text{-}C(^nBu)NR]$ (R = ^tBu, C_6H_{11}, $C_6H_3Me_2$-2,6). Reaction of Cp^*UMe_2 with CN^tBu gave $Cp^*{}_2UX[\eta^2\text{-}C(Me)N^tBu]$.

Cramer, et al.[231] reported the insertion of acetonitrile into Cp_3U $CHPMePh_2$ to produce $Cp_3UNC(Me)CHPMePh_2$ (Figure 68). The U-N bond is a very short 2.06(1)Å and the U-N-C angle is 163(1)°. Other bonding parameters suggest multiple bonding character for the U-N interaction between 2 and 3 and a highly delocalized π system.

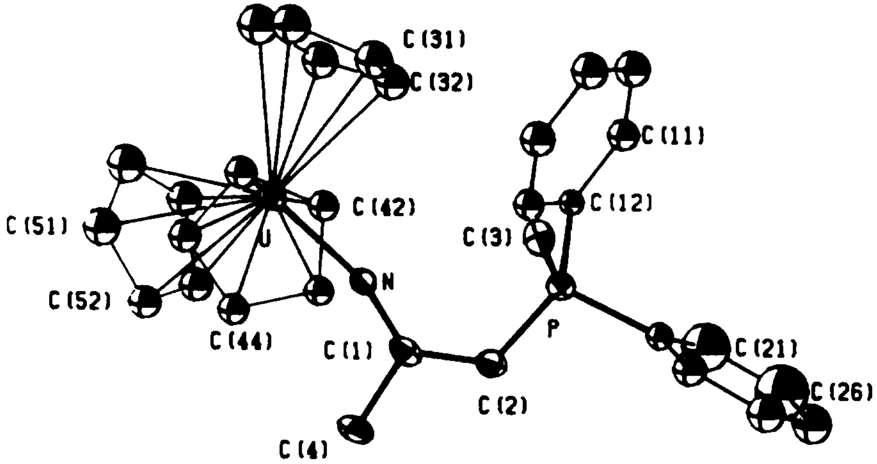

Fig. 68. $Cp_3UNC(Me)CHPMePh_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1984 American Chemical Society.)

Ossola, et al.[232] discussed in some detail the protolytic cleavage of An(U, Th)-N bonds by cyclopentadiene. Both $U(NEt_2)_4$ and $Th(NEt_2)_4$ were treated stoichiometrically with HCp and kinetically controlled to form $CpAn(NEt_2)_{4-n}$ ($n = 2, 3$ for U and $n = 1\text{-}3$ for Th). Excess HCp for M = U produced Cp_4U.

Andersen and Brennan[233] reported the reactions of $(CpMe)_3U(THF)$ with organic azides to give $(CpMe)_3UNR$ and with organic isocyanates to yield $[(CpMe)_3U]_2[PhNCO]$. Crystallographic characterizations of $(CpMe)_3UNPh$ (Figure 69) and $[(CpMe)_3U]_2[PhNCO]$ (Figure 70) were carried out. In the former, the U-N distance of 2.019(6)Å and U-N-C angle of 167.4° suggest a U-N triple bond. In the latter the $[PhNCO]^{2-}$ anion bridges two $[(CpMe_3)U]^+$ fragments in an η^1, η^2 fashion. Important distances include U-N = 2.36(2)Å, U-C = 2.42(2)Å, U-O = 2.11(1)Å.

Sonnenberger, Morss and Marks[234] reported Th-L bond disruption enthalpies for Cp_3ThR compounds by anaerobic batch-titration solution calorimetry from enthalpies of solution of the complexes in toluene followed by enthalpies of

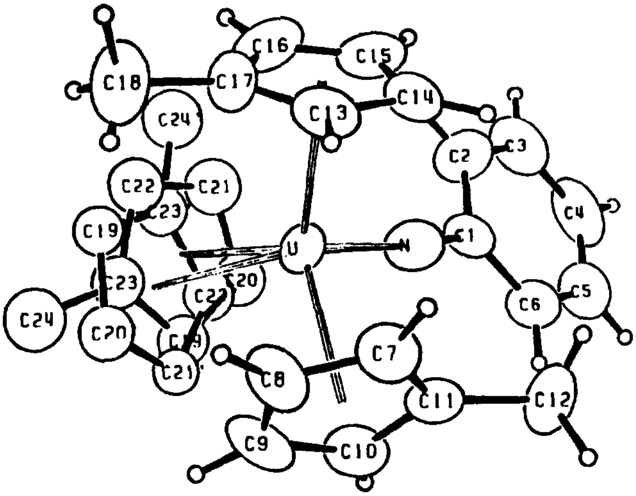

Fig. 69. $(CpMe)_3UNPh$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1985 American Chemical Society.)

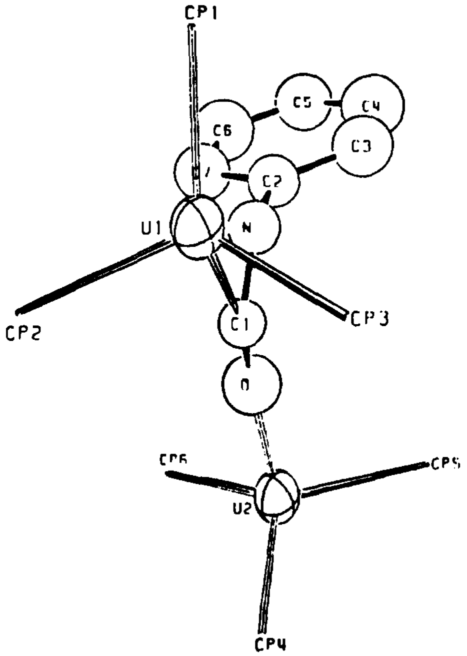

Fig. 70. $[(CpMe)_3U]_2[PhNCO]$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1985 American Chemical Society.)

alcoholysis with CF_3CH_2OH. The D(Th-R) gas values reported include: CH_2SiMe_3, 86.1 kcal/mol; Me, 82.7 kcal/mol; CH_2CMe_3, 77.9 kcal/mol; CH_2Ph, 77.9 kcal/mol; and $CHMe_2$, 77.3 kcal/mol.

Sonnenberger, Mintz and Marks[235] published a synthetic and kinetic study of CO migratory insertion for Cp_3ThR (R = ^iPr, ^sBu, neopentyl, ^nBu, CH_2SiMe_3, Me, CH_2Ph). The reactions were observed to be first order in Cp_3ThR and first order in CO. η^2-acyls were isolated for R = Me, ^iPr, ^nBu, neopentyl, and ^sBu. Enolate rearrangement products were isolated for R = ^iPr and CH_2SiMe_3. A comparative study of CO_2 migratory insertion was also discussed.

Rossetto, et al.[236] reported the reaction of Cp_3UR (R = Me, Et) in toluene at room temperature with LBH_3 (L = BH_3, THF, Me_2S) to give $Cp_3U(BH_4)$. Where L was a stronger Lewis base than BH_3, BH_3 attack of Cp_3UR was not observed.

Arnaudet, et al.[237] reported the reduction of Cp_3U^nBu to $Cp_3U^nBu^-$ and its isolation as a $Li[2.1.1]^+$ cryptate salt. The crystal structure (Figure 71) revealed a U^{3+} environment very similar to the neutral U^{4+} compound. Important parameters include U-C(η^5) = 2.83Å and U-C(σ) = 2.557(9)Å.

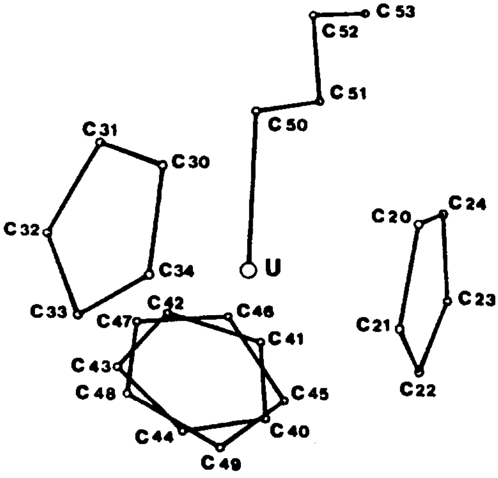

Fig. 71. $[Cp_3U^nBu]^-$ anion. (Reprinted with permission from Organometallics. Copyright 1986 American Chemical Society.)

Brennan, Andersen, and Zalkin[238] observed the reactions of the trivalent species $(CpMe)_3U(THF)$ and Cp'_3U with CS_2 to form the binuclear U^{4+} complexes $[(CpR)_3U]_2[\mu\text{-}\eta^1,\eta^2\text{-}CS_2]$ (R = Me, $SiMe_3$). The crystal structure of R = Me (Figure 72) revealed disorder of the CS_2 group resulting in equivalent η^1, η^2 U-S distances of 2.792(3). The U-C distance is 2.52(2)Å.

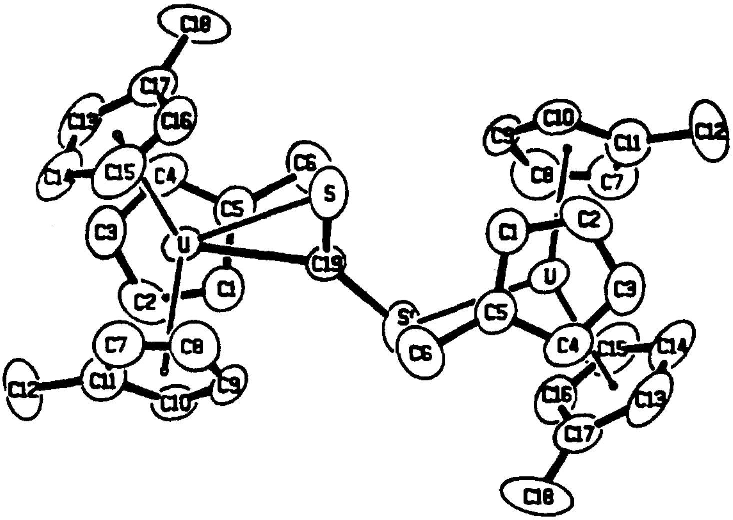

Fig. 72. $[(CpMe)_3U]_2[\mu\text{-}\eta^1,\eta^2\text{-}CS_2]$. (Reprinted with permission from Inorganic Chemistry. Copyright 1986 American Chemical Society.)

Ossola, et al.[239] synthesized Cp_3UAlH_4 by the reaction of Cp_3UBH_4 and $LiAlH_4$ in OEt_2. A polymeric structure with trigonal planar Cp_3U moieties bridged by AlH_4 groups was proposed.

Baudry and Ephritikhine[240] reported the synthesis of $L_2ReH_6UCp_3$ (L = PPh_3, $P(p\text{-}FPh)_3$ via the reactions of $K[L_2ReH_6]$ with Cp_3UCl.

Preliminary results of an investigation on the electronic structures of Cp_3UX (X = F, Cl, Br) complexes studied with He(I)/He(II) UV photoelectron spectroscopy and non relativistic DV-Xα first principal molecular orbital calculations were published by Vittadini, et al.[241]

(iii) Biscyclopentadienyl compounds. A tremendous amount of activity was once again observed in the preparation of biscyclopentadienyl compounds of the actinides. Sonnenberger and Gaudiello observed a one electron reversible reduction in CH_3CN at $E_{1/2}$ = -0.68 V for $Cp^*{}_2NpCl_2$.[242] The compound was prepared by the reaction of $NpCl_4$ with $Cp^*MgCl(OEt_2)$.

Lappert, et al.[243] prepared the complete series of uranium(III) biscyclopentadienyl halides: $[Cp''_2UX]_n$ (X = F, Cl, Br, I) by reduction of the corresponding U^{4+} dihalides with Na/Hg in toluene. The flouride was prepared by reduction of $[Cp''_2U(\mu\text{-}BF_4)\mu\text{-}F]_2$. The isostructural chloro- and bromo-derivatives were structurally characterized (Figure 73) and shown to be dimeric. The U···U separation is 4.357(1)Å with symmetric bridges: U-Cl = 2.818(4)Å, U-Cl' = 2.802(4)Å.

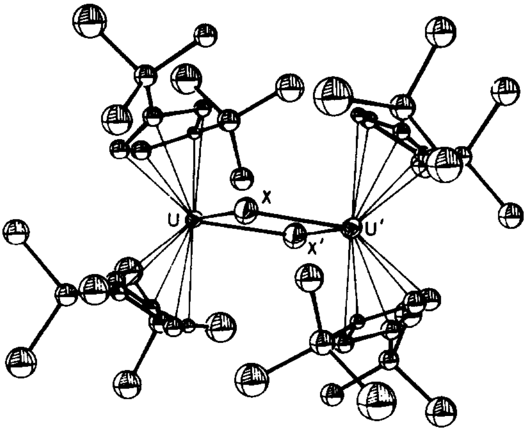

Fig. 73. [Cp"U(μ-X)]$_2$. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

Ryan and Sattelberger, et al.[244] utilized Cp*$_2$Th(PPh$_2$)$_2$ to prepare a complex containing a Th-Pt bond by reaction with Pt(1,5-cyclooctadiene)$_2$ in toluene and in the presence of PMe$_3$. The complex, Cp*$_2$Th(PPh$_2$)$_2$Pt(PMe$_3$), was structurally characterized and is shown in Figure 74. The Th-Pt distance is 2.984(1)Å. The PPh$_2$ groups bridge the two metal atoms.

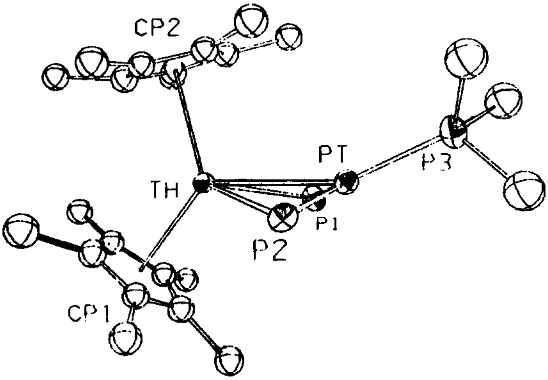

Fig. 74. Cp*$_2$Th(PPh$_2$)$_2$Pt(PMe$_3$). (Reprinted with permission from Journal of the American Chemical Society. Copyright 1986 American Chemical Society.)

Marks, et al.[245] prepared $Cp^*_2ThIRuCp(CO)_2$, a compound with an unsupported/unbridged Th-Ru bond, by reaction of $Cp^*_2ThX_2$ (X = Cl, I) with Na-$[CpRu(CO)_2]$. The structure is shown in Figure 75. The Th-Ru bond is 3.0277(6)Å.

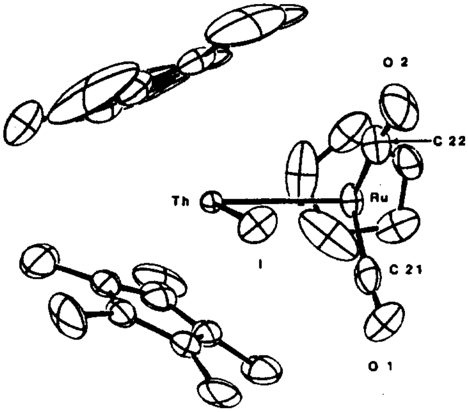

Fig. 75. $Cp^*_2ThIRuCp(CO)_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1985 American Chemical Society.)

The polysulfide $Cp^*_2ThS_5$ was prepared by Ryan, et al.[246] via the reaction of $Cp^*_2ThCl_2$ with Li_2S_5 (the latter generated by reaction of S with $LiBHEt_3$ in THF). The structure (Figure 76) revealed an unusual twist-boat conformation of the ThS_5 ring.

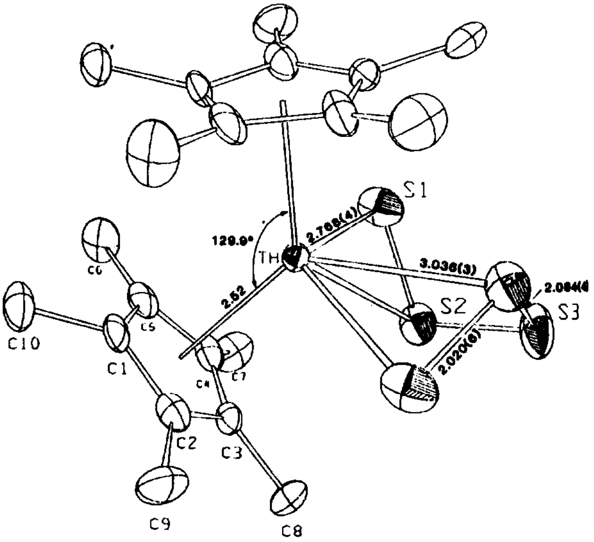

Fig. 76. $Cp^*_2ThS_5$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1986 American Chemical Society.)

Ryan, et al.[247] reported the preparation of the first diorganophosphido actinide complexes, $Cp^{*}_2Th(PR_2)_2$ (R = Ph, Cy, Et), prepared by reaction of $Cp^{*}_2ThCl_2$ with $LiPR_2$. The diphenyl phosphido complex was crystallographically characterized (Figure 77). The P atoms occupy pseudotetrahedral sites and show no evidence of Th-P multiple bonding. The Th-P distances average 2.87(2)Å.

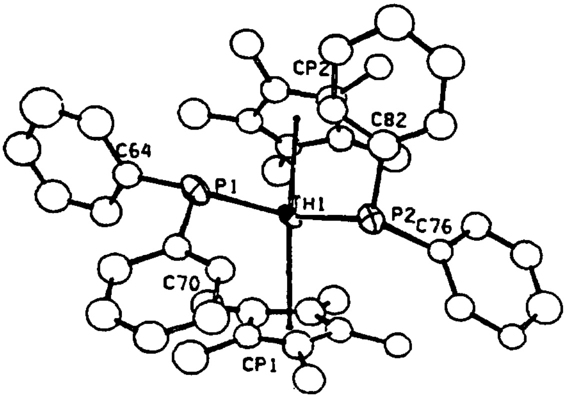

Fig. 77. $Cp^{*}_2Th(PPh_2)_2$. (Reprinted with permission from Organometallics. Copyright 1986 American Chemical Society.)

Ryan, et al.[248] further utilized this compound in reaction with Ni(1,5 cyclooctadiene)$_2$ in THF under CO to produce $Cp^{*}_2Th(PPh_2)_2Ni(CO)_2$. The phosphido bridged structure (Figure 78) exhibits a Th-Ni separation of 3.206(2)Å, 0.5Å less than the expected nonbonded distance. Ortiz[249] carried out MO calculations on this Th-Ni interaction by modeling $Cp^{*}_2Th(PH_2)_2Ni(CO)_2$. A weak donor-acceptor relationship between the Ni and Th centers was proposed.

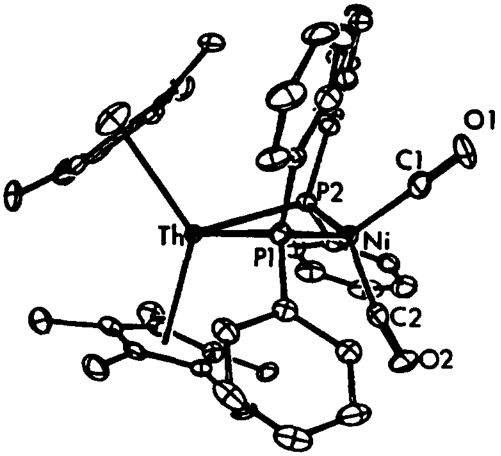

Fig. 78. $Cp^{*}_2Th(PPh_2)_2Ni(CO)_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1985 American Chemical Society.)

Marks, Day and Duttera[250] published an account of the reaction chemistry of $[Cp^*_2AnH_2]_2$ (An = Th, U) with trimethyl phosphite. Transposition of hydride and methoxide ligands yielded $Cp^*_2An(OMe)_2$ and $[Cp^*_2An(OMe)]_2PH$ complexes. The structure of $[Cp^*_2U(OMe)]_2PH$ was determined and is shown in Figure 79. The U-P-U bridge is symmetric with U-P = 2.743(1)Å and U-P-U = 157.7(2)°.

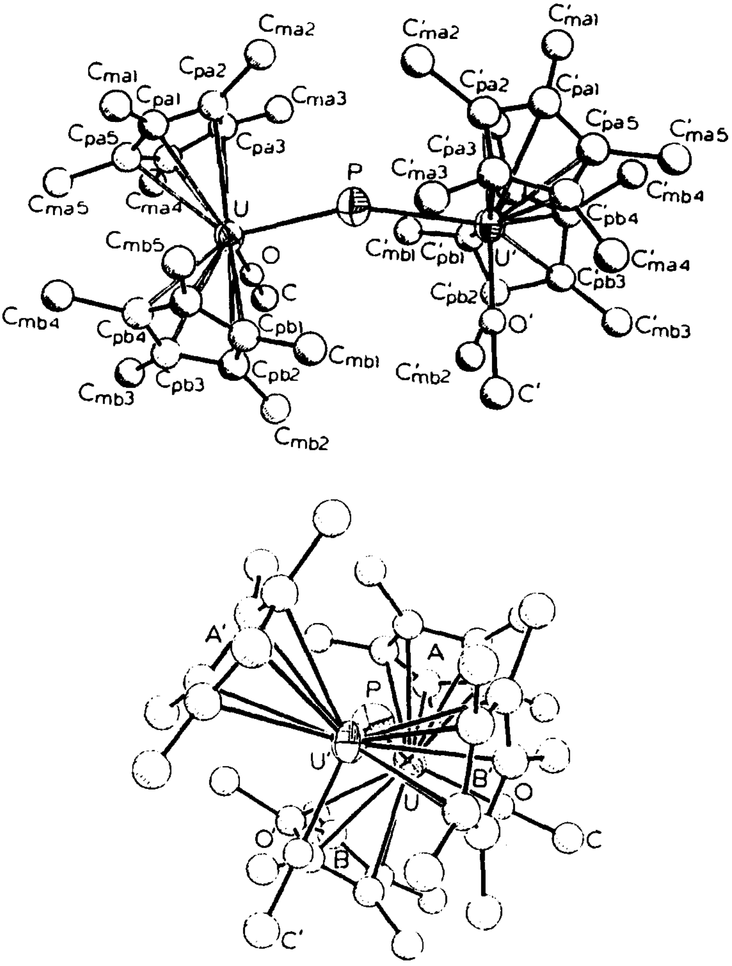

Fig. 79. $[Cp^*_2U(OMe)]_2PH$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1984 American Chemical Society.)

The dimer, $[Cp"_2U(BF_4)(F)]_2$, was prepared by the reaction of $Ag[BF_4]$ in OEt_2 with $Cp"_2UCl_2$ or $Cp"_2U(CH_2R)_2$ (R = $SiMe_3$, Ph) and structurally characterized (Figure 80).[251] The bridging fluorides are not symmetrical at 2.354(5) and 2.260(5)Å from U. The bridging BF_4^- ligands are 2.402(5) and 2.420(5)Å from U.

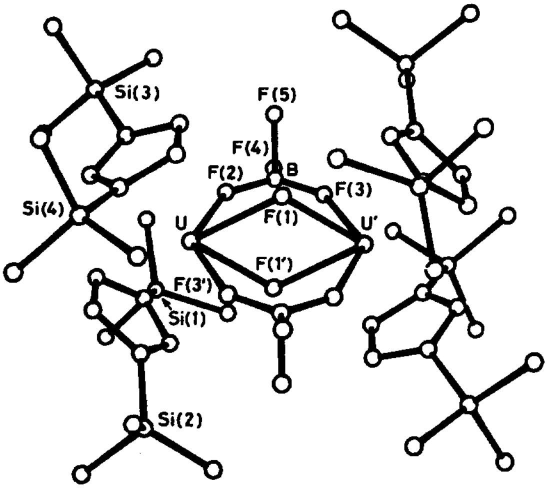

Fig. 80. $[Cp"_2U(BF_4)(F)]_2$. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

Berton, et al.[252] reported the synthesis of dialkoxide and diaryloxides of U(IV) by cleavage of U-NEt_2 in $Cp_2U(NEt_2)_2$ with ROH and ArOH. Yields were observed to be dependent on the bulk of the OR or OAr groups. The products also underwent disproportionation reactions to from Cp_3U derivatives.

The amide, $Cp_2U(NEt_2)_2$ was shown to react with 8-hydroxyquinoline to form Cp_2U(8-hydroxyquinolate)$_2$. Attempts by Zanella, et al.[253] to prepare this compound via the reaction of UCl_2(8-hydroxyquinolate)$_2$ with TlCp produced Cp_3UCl instead.

Day and Klemperer, et al.[254] prepared and characterized $[N(^nBu)_4]_4$-$[Cp_2U(TiW_5O_{19})]_2$ (Figure 81). Two polyoxoanions are bridged by the Cp_2U^{2+} groups.

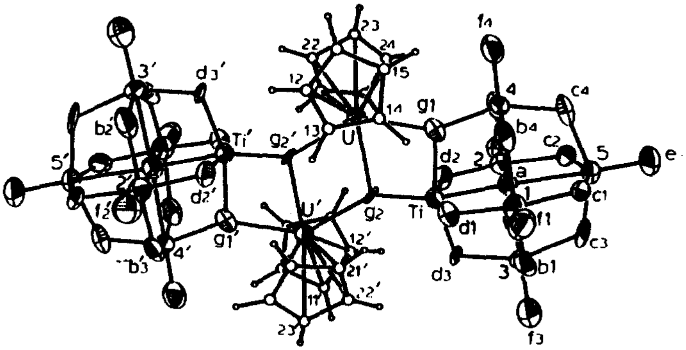

Fig. 81. $[Cp_2U(TiW_5O_{19})]_2^{4-}$ anion. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1985 American Chemical Society.)

Zanella, et al.[255] studied the coordination of tropolonate with thorium(IV) and uranium(IV) chlorides. In this paper four organometallic products were prepared: $CpU(tropolonate)_3$, $Cp_2U(tropolonate)_2$, $CpU(tropolonate)Cl_2$, and $CpU(tropolonate)_2Cl$.

Bulky N,N'-di-p-tolyltriazenide (triaz) and N,N'-di-p-tolylformamidide (form) were utilized by Paolucci, Zanella, and Berton[256] to stabilize Cp_2AnL_2 (An = Th, U) compounds. The compounds $Cp_2An(triaz)_2$ (An = Th, U) and $Cp_2U(form)_2$ were characterized by elemental analysis, ^1H NMR, and mass spectral studies.

Marks and Moloy[257] published an elegant account of migratory CO insertion reactions into Th-C and Th-H bonds. The compounds Cp^*_2ThRX (R = H, D, Me, ^nBu, $CH_2{}^tBu$; X = OCH^tBu_2, OC_6H_3-2,6-$^tBu_2$ and O^tBu) were prepared, characterized and reacted with CO to form η^2-acyls and η^2-formyls. Labeling, crossover experiments and rate data were used to compare the Th-C versus Th-H insertions.

Tatsumi, et al.[258,259] studied the electronic and geometric structures of these same type of acyl complexes. Comparisons between the η^2-aryls formed and η^1-coordination were discussed, as well as the unique reactivity of acyl ligands in $Cp_2An(COR)X$ compounds. Detailed comparisons with Cp_2Ti^- and $Cp_2Zr(\eta^2\text{-acyl})$ compounds were also presented.

Marks, et al.[260] reported the carbonylation of $Cp^*_2ThCl(\eta^2\text{-}COCH_2{}^tBu)$ in the presence of phosphines to yield the ylide, $Cp^*_2Th[OC(CH_2{}^tBu)C(PR_3)O]Cl$ (R = Me, Ph). Without the phosphines the enedionediolate, $\{Cp^*_2Th[OC(CH_2{}^tBu)CO]Cl\}_2$ was formed. The acyl complexes, $Cp^*_2ThCl(COR)$ (R = $CH_2{}^tBu$, CH_2Ph), reacted with isocyanides (RNC, R = ^tBu, C_6H_{11}, 2,6-$Me_2C_6H_3$) to form ketenimine complexes, $Cp^*_2Th[OC(CH_2{}^tBu)CNR]Cl$ and $Cp^*_2Th[OC(CH_2Ph)CNR]Cl$. The adducts, $Cp^*_2Th[OC(CH_2{}^tBu)CNR](CNR)Cl$ and $Cp^*_2Th[OC(CH_2Ph)CNR](CNR)Cl$, were formed upon addition of a second equivalent of isocyanide. Structural characterizations of $\{Cp^*_2Th[OC(CH_2{}^tBu)CO]Cl\}_2$ (Figure 82), $Cp^*_2Th[OC(CH_2{}^tBu)C(PMe_3)O]Cl$ (Figure 83), $Cp^*_2ThCl[OC(CH_2{}^tBu)CN(2,6\text{-}Me_2C_6H_3)]$ (Figure 84), $Cp^*_2ThCl(C_{22}H_{24}N_2O)$ (Figure 85) and $Cp^*_2Th[OC(CPh_2)C(CH_2{}^tBu)O]Cl$ (Figure 86) were carried out.

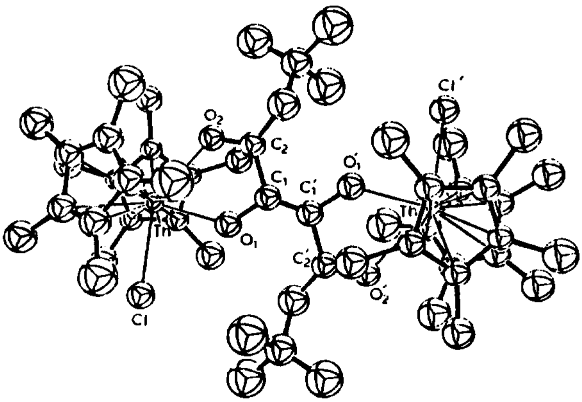

Fig. 82. $\{Cp^*_2Th[OC(CH_2{}^tBu)CO]Cl\}_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1986 American Chemical Society.)

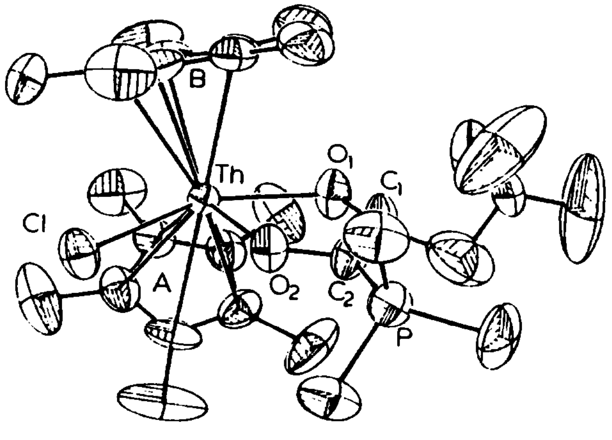

Fig. 83. $Cp^*_2Th[OC(CH_2{}^tBu)C(PMe_3)O]Cl$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1986 American Chemical Society.)

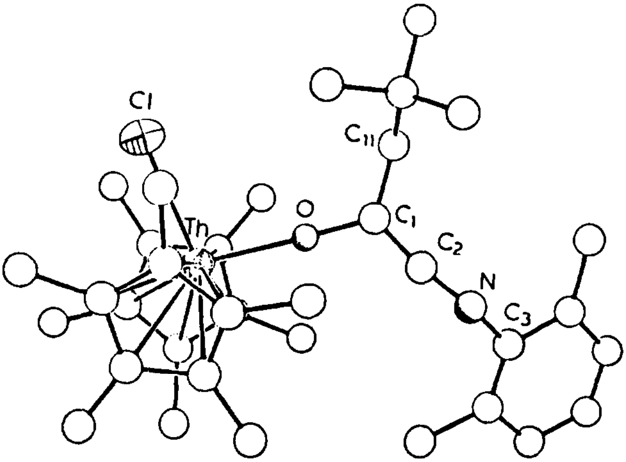

Fig. 84. $Cp^*_2ThCl[OC(CH_2{}^tBu)CN(2,6\text{-}Me_2C_6H_3)]$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1986 American Chemical Society.)

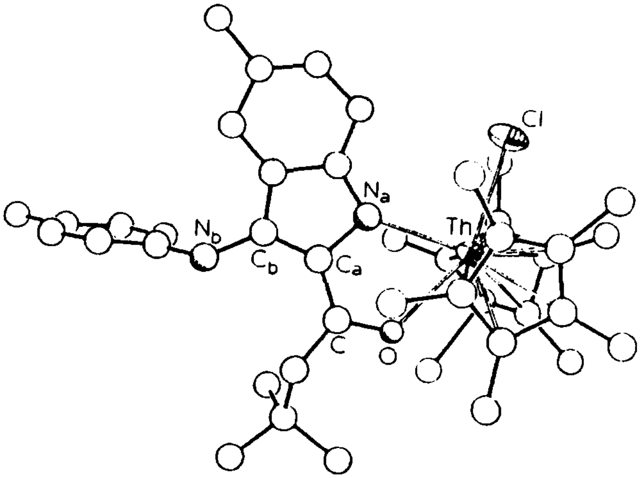

Fig. 85. $Cp^*_2ThCl(C_{22}H_{24}N_2O)$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1986 American Chemical Society.)

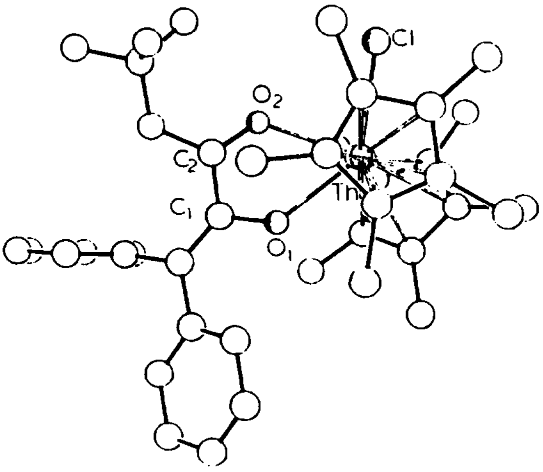

Fig. 86. $Cp^{*}{}_2Th[OC(CPh_2)C(CH_2{}^tBu)O]Cl$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1986 American Chemical Society.)

Marks and Moloy[261] further discussed this chemistry with a contribution on the insertion of CO_2 into An-Me and An-H bonds. The insertion products, $Cp^{*}{}_2An(OAc)_2$ (An = Th, U), were prepared by the reactions of excess CO_2 with $Cp^{*}{}_2AnMe_2$. The compounds were also directly prepared from $Cp^{*}{}_2AnCl_2$ and NaOAc. Control of the CO_2 addition resulted in the monoinsertion compounds $Cp^{*}{}_2AnMe(OAc)$. When $Cp^{*}{}_2Th(H)(OCH^tBu)$ was reacted with CO_2, $Cp^{*}{}_2Th(O_2CH)(OCH^tBu)$ was formed.

Tatsumi, Hofmann, Hoffmann, and Marks, et al.[262] published a detailed account of a theoretical and experimental study of double carbonylation of $Cp^{*}{}_2An^{2+}$ complexes. A complete mechanistic study of the double carbonylation and C=C bond formation to give monomeric or dimeric $Cp^{*}{}_2An^{2+}$ complexes of cis-enedialato ligands was reported.

Dormond, et al.[263,264] published two accounts of the insertion of isocyanides into U-N bonds. The compounds, $Cp_2U(NEt_2)_2$ and $Cp^{*}{}_2U(NEt_2)Cl$, were reported to readily react with isocyanides to give iminoalkylamido insertion compounds.

Marks and Toscano[265,266] presented a high resolution ^{13}C NMR study of $Cp^{*}{}_2ThMe_2$ and $[Cp^{*}{}_2Th(\mu\text{-}H)H]_2$ adsorbed on partially dehydroxylated or dehydroxylated γ-alumina. The technique proved capable of probing the adsorbate-alumina interaction and indicated transfer of the methyl groups from thorium to the surface aluminum sites. The products were surface Si-Me and Cp*$_2$ThMe-(siloxide) functionalities.

Another report by these authors and others[267] detailed the surface chemistry of Cp*$_2$AnMe$_2$ and Cp*$_2$An(CD$_3$)$_2$ (An = Th, U) on alumina supports and compared the catalytic chemistry to the solution chemistry of these compounds. Methane-evolving surface reaction pathways were identified as An-Me protolysis via surface OH, Cp* H atom abstraction and intramolecular elimination of methane.

Marks and Sonnenberger, et al.[268] determined the An-L (An = Th, W) bond disruption enthalpies for Cp*$_2$MRX compounds (R = alkyl, aryl, hydride; X = alkyl, chloride, alkoxide). Alkoxide ancillary ligands appeared to strengthen the An-R bond.

Marks, et al. studied the reversible cyclometalation of Cp*$_2$Th-(CH$_2$SiMe$_3$)$_2$.[269] The authors were able to quantify the thermodynamic and kinetic factors during the reaction.

A further report by Marks and Schultz, et al.[270] discussed the syntheses, structures and cyclometalation reactions of Cp*$_2$Th dialkyls. The neutron diffraction crystal structure of Cp*$_2$Th(CH$_2$CMe$_3$)$_2$ was determined (Figure 87). The neopentyl ligands are highly unsymmetrical. The Th-C and Th-C-C parameters for the two ligands are 2.543(4)Å, 132.1(3)° and 2.456(4)Å, 158.2(3)° and reflect steric congestion. An agostic Th-H interaction was suggested. The new compounds prepared included Cp*$_2$Th(CH$_2$CMe$_2$CH$_2$), Cp*$_2$Th(CH$_2$SiMe$_2$CH$_2$), Cp*$_2$Th-(CH$_2$CMe$_3$)(CH$_2$SiMe$_3$), Cp*$_2$Th(CH$_2$CMe$_2$Et)$_2$, Cp*$_2$Th(CH$_2$CMeEtCH$_2$), Cp*$_2$Th(CH$_2$Si-Me$_2$Ph)$_2$, Cp*$_2$Th(CH$_2$SiMePhCH$_2$) and Cp*$_2$Th(CH$_2$SiMe$_2$-o-C$_6$H$_4$). The X-ray crystal structures of Cp*$_2$Th(CH$_2$SiMe$_2$-o-C$_6$H$_4$) (Figure 88) and Cp*$_2$Th(CH$_2$CMe$_3$)(CH$_2$SiMe$_3$) (Figure 89) were also reported.

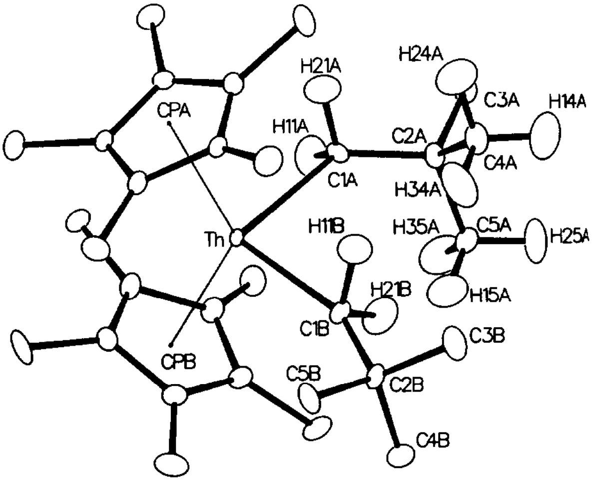

Fig. 87. $Cp^{*}_{2}Th(CH_2CMe_3)_2$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1986 American Chemical Society.)

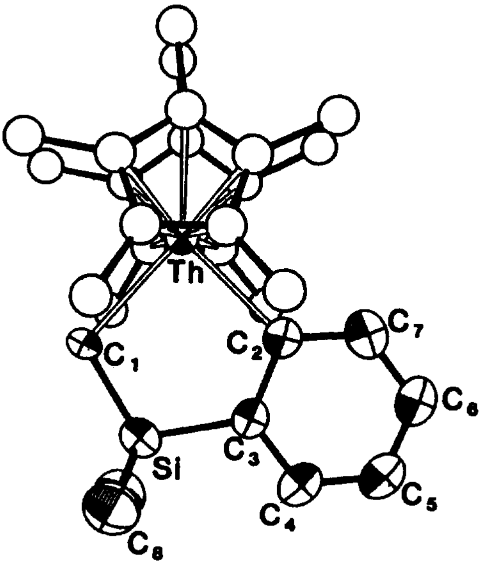

Fig. 88. $Cp^{*}_{2}Th(CH_2SiMe_2\text{-}o\text{-}C_6H_4)$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1986 American Chemical Society.)

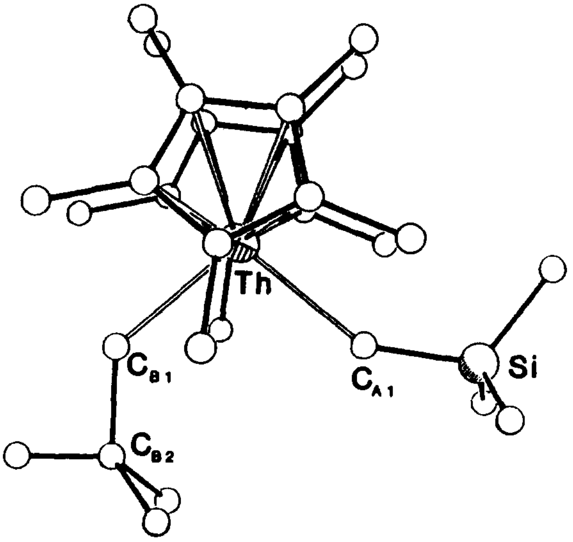

Fig. 89. $Cp^{*}_{2}Th(CH_2CMe_3)(CH_2SiMe_3)$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1986 American Chemical Society.)

Marks and Fendrick[271,272] discussed in detail the ring opening reactions of thoracyclobutanes with saturated hydrocarbons and related molecules (RH) to give $Cp^{*}_{2}ThR(CH_2CMe_3)$. Relative rates of the R-H functionalities were reported to be $SnMe_4 \geq SiMe_4 >$ cyclopropane $\approx PMe_3 >$ benzene $> CH_4 \geq C_2H_6 \gg$ cyclohexane. Further reaction in the case of $SiMe_4$, $SnMe_4$ and PMe_3 yielded $Cp^{*}_{2}Th(CH_2SiMe_2CH_2)$, $Cp^{*}_{2}Th(CH_2SnMe_2CH_2)$ and $Cp^{*}_{2}Th(CH_2PMeCH_2)$. A heterolytic four-center mechanistic pathway was postulated for the Th^{4+} C-H activation.

Marks and Day, et al.[273] reported the syntheses and chemistry of $Cp^{*}_{2}An(\eta^4\text{-}C_4H_6)$, (An = Th, U) and $Cp^{*}_{2}Th(\eta^4\text{-}CH_2CMeCMeCH_2)$. The crystal structure of $Cp^{*}_{2}Th(\eta^4\text{-}C_4H_6)$ was determined. The observed Th-C(terminal butadiene atoms) and Th-C(internal butadiene atoms) averaged 2.57 and 2.74Å, respectively. Th-butadiene bond disruption energies were also presented.

Erker, et al.[274] also reported the synthesis of $Cp^{*}_{2}Th(\eta^4\text{-}C_4H_6)$ from $Cp^{*}_{2}ThCl_2$ and magnesium butadiene. Coupling of this compound with a carbonyl ligand of chromium hexacarbonyl produced a thorium oxycarbene chromium complex.

Marks and Day, et al.[275] published the synthesis of the chelating ligand $Me_2Si(Cp^{*})_2^{2-}$ and its reaction with $ThCl_4$. The compounds $Me_2Si(Cp^{*})_2ThR_2$ (R = ^{n}Bu, CH_2CMe_3, CH_2SiMe_3, $CH_2C_6H_5$ and C_6H_5 were synthesized. The crystal structure of $Me_2Si(Cp^*)_2Th(CH_2SiMe_3)_2$ was determined (Figure 90). The centroid-Th-centroid angle is only 118.4°.

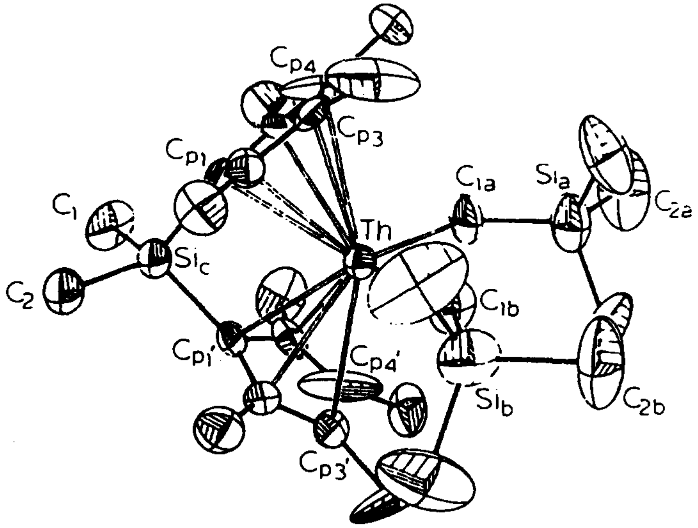

Fig. 90. $Me_2Si(Cp^*)_2Th(CH_2SiMe_3)_2$. (Reprinted with permission from Organometallics. Copyright 1984 American Chemical Society.)

(iv) Monocyclopentadienyl compounds. Benetollo, *et al.*[276] published the crystal structures of $CpUCl_3(OPPh_3)_2 \cdot THF$ (Figure 91) and $CpUCl_3(OP(NMe_2)_3)_2$ (Figure 92). Each uranium site features octahedral coordination with the phosphine oxide in *cis* orientation, *mer*-chloride ions, and the Cp ligand *trans* to one oxide.

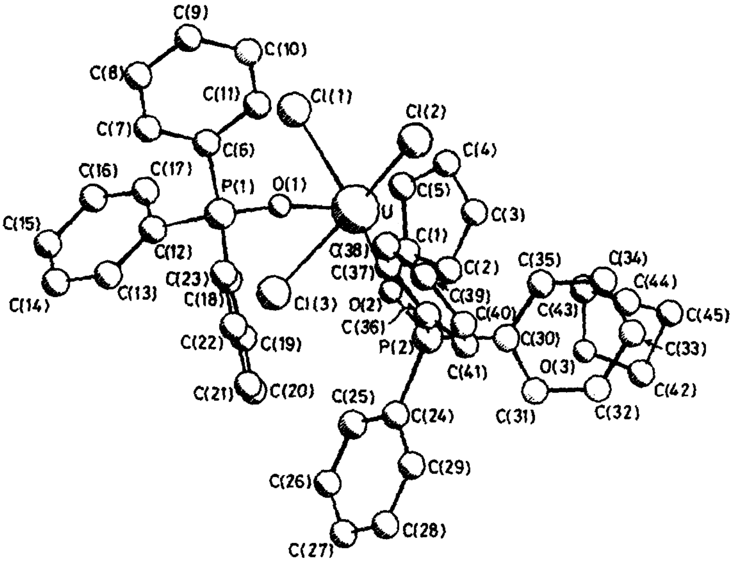

Fig. 91. $CpUCl_3(OPPh_3)_2 \cdot THF$. (Reprinted with permission from Journal of the Chemical Society, Dalton Transactions.)

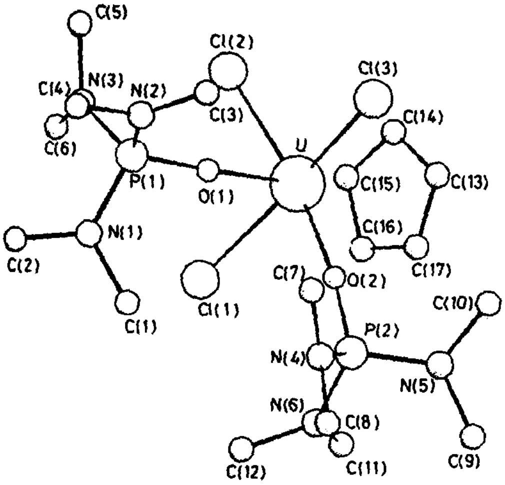

Fig. 92. $CpUCl_3(OP(NMe_2)_3)_2$. (Reprinted with permission from Journal of the Chemical Society, Dalton Transactions.)

Bagnall and Alcock, et al.[277] reported the synthesis of $CpNpCl_3L_2$ (L = dimethylformamide, $MeCON^iPr_2$, $OPMe_3$, $EtCON^iPr_2$, $OPMe_2Ph$, $OPMePh_2$) and the crystal structure (Figure 93) of L = $OPMePh_2$. The same arrangement of ligands was observed as found for the U compounds above.[276] The Np-Cl and Np-O separations average 2.65(2) and 2.27(5)Å, respectively.

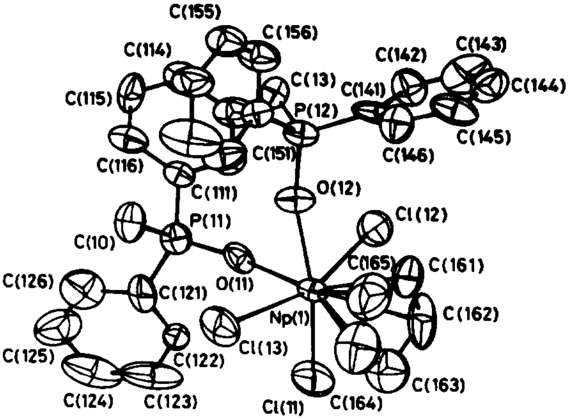

Fig. 93. $CpNpCl_3(OPMePh_2)_2$. (Reprinted with permission from Journal of the Chemical Society, Dalton Transactions.)

Several other publications by Bagnall and coworkers made contributions to this area. The synthesis, IR and near IR spectra were reported for $CpPuCl_3L_2$[278] (L = $HCONMe_2$, $MeCONMe_2$, $MeCON^iPr_2$, $EtCON^iPr_2$, $Me_3CCONMe_2$, $OPMe_3$, $OPMe_2Ph$, $OPMePh_2$, OPh_3, $OP(NMe_2)_3$), $CpAn(NCS)_3L_x$[279] (x = 2, An = Pu, L = $OPMe_3$; An = Np, Pu, L = $OPMe_2Ph$, $OPMePh_2$, $OPPh_3$; x = 3, An = Np, L = $OPMe_3$), $An(NCS)_4L_4$[279] (An = Np, Pu, L = $OPMe_2Ph$, $OPMePh_2$), $CpThX_3L_2$[280] (X = Cl, L = $MeCON^iPr_2$, $MeCON(C_6H_{11})_2$, $EtCON^iPr_2$, $Me_2CHCONMe_2$, $Me_2CHCON^iPr_2$, $Me_3CCONMe_2$, $CO(NMe_2)_2$, $Me_2NCON(CH_2CHMe_2)_2$; X = Br, L = $Me_2CHCONMe_2$, $Me_2CHCON^iPr_2$, $EtCONEt_2$), $CpUCl_3L_2$[279] (L = $MeCON^iPr_2$, $EtCON^iPr_2$, $CO(NMe_2)_2$), $CpUCl_3(MeCON(C_6H_{11})_2)_2(THF)$[280], $CpAnCl_2(HBL_3)$[281] (An = Th, U; L = 3,5-dimethylpyrazolyl), $CpThCl_3L_x$[282] (x = 2, L = THF; x = 3, L = MeCN), $(CpMe)ThCl_3(THF)_2$,[282] $CpUCl_3L_2$[282] (L = $OPMe_3$, $OPMe_2Ph$, $OPMePh_2$), and $CpU(NCS)_3L_3$[282] (L = $OPMe_2Ph$, $OPMePh_2$). A diphenylphosphinopyridine adduct of $CpUCl_3$ was reported by Wassermann, et al.[283]

Le Marechal, et al.[284] described the dynamic solution behavior of some of these compounds ($CpUCl_3L_2$ L = hexamethylphosphoramide, THF, $OPPh_3$). The stable structure in solution was determined to be a mer pseudo-octahedral configuration.

Cramer and Gilje, et al.,[285] published the crystal structure of $CpU[(CH_2)(CH_2)PPh_2]_3$ (Figure 94). The Cp centroid and one CH_2 group occupy axial positions in a pseudo-pentagonal bipyramidal geometry. The U-C(σ) bonds are long at 2.66(3)Å.

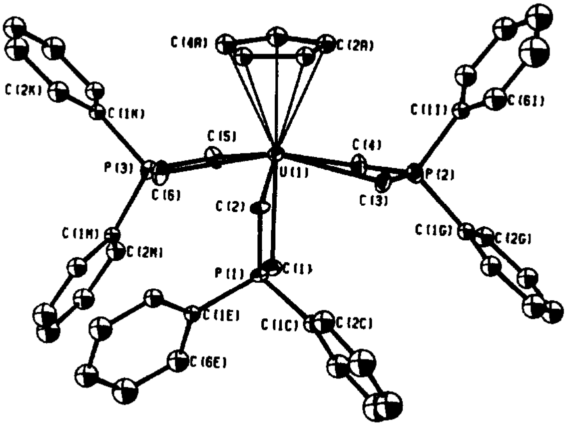

Fig. 94. $CpU[(CH_2)(CH_2)PPh_2]_3$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1984 American Chemical Society.)

Baudry, et al.[286] reported the crystal structure of $CpU(BH_4)_3$ (Figure 95). The U-B distances (2.46(4) and 2.57(5)Å) suggest tridentate coordination, although the hydrogen atoms were not located.

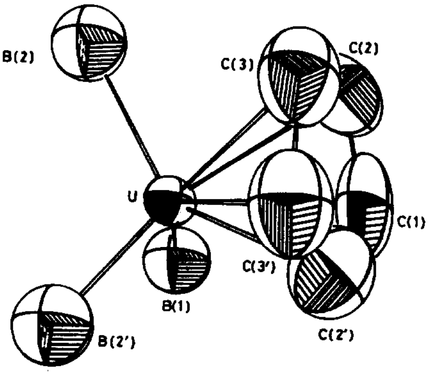

Fig. 95. $CpU(BH_4)_3$. (Reprinted with permission from Journal of the Chemical Society, Chemical Communications.)

(v) Indenyl compounds. Five contributions appeared discussing the chemistry of actinide idenyl compounds each involving crystallographic investigations. Rebizant, *et al.*[287] published the crystal structure of Th(Ind)$_4$ (Figure 96). The Th-C distances suggest a trihapto coordination of the indenyl ligands. Trihapto coordination was also observed for [U(Ind)Br$_2$-(CH$_3$CN)$_4$]$_2$[UBr$_6$] (Figure 97).[288] The U-C1,C2,C3 distances are 2.63(4), 2.67(4), and 2.69(4)Å, respectively while the U-C8,C9 separations are much longer at 2.81(4) and 2.82(4)Å.

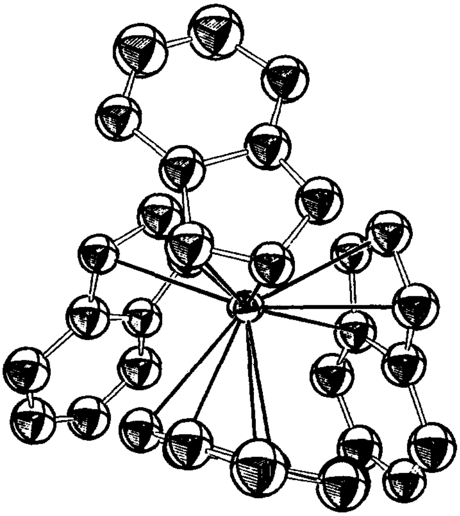

Fig. 96. Th(Ind)$_4$. (Reprinted with permission from Journal of the Less-Common Metals.)

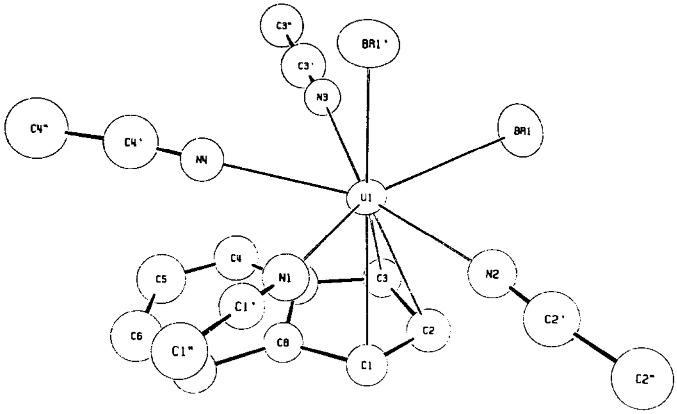

Fig. 97. $[U(Ind)Br_2(CH_3CN)_4]^+$ cation. (Reprinted with permission from Lanthanide and Actinide Research.)

Pentahapto coordination was found in the structure of $U(Ind)Br_3(THF)_2$ (Figure 98, Rebizant, Spirlet and Goffart[289]). The U-C(η^5) separations range from 2.68(2)Å (C(3)) to 2.79(2)Å (C(8)).

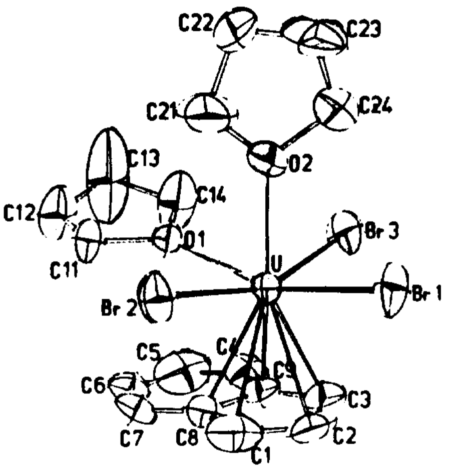

Fig. 98. $U(Ind)Br_3(THF)_2$. (Reprinted with permission from Acta Crystallography.)

Meunier-Piret and Van Meerssche[290] published the structure of U(1,4,7-trimethylindenyl)$_3$Cl. The indenyl ligand is η^5-coordinated to uranium.

Beeckman, et al.[291] prepared a large series of indenyl compounds by *reaction of An(Ind)X_3(THF)$_2$ with pure methyl cyanide. The compounds prepared* included AnLCl_3(THF)$_2$ (An = Th, U, L = 1-ethylindenyl, 1,4,7-trimethylindenyl; An = Th, L = 1,2,3,4,5,6,7-heptamethylindenyl), [AnLX_2(CH_3CN)$_4$][AnX_6] (An = Th, U, X = Cl, L = indenyl, 1-ethylindenyl, 1,4,7-trimethylindenyl; An = Th, X = Cl, L = 1,2,3,4,5,6,7-heptamethylindenyl; An = U, X = Br, L = indenyl), AnLX_3($CH_3CH_2CH_2CN$)$_2$ (An = U, X = Br, L = indenyl, 1-ethylindenyl; An = Th, U, X = Cl, L = 1-ethylindenyl; An = Th, X = Cl, L = 1,2,3,4,5,6,7-heptamethylindenyl), and AnLCl_3(C_6H_5CN)$_2$ (An = Th, X = Cl, L = 1,2,3,4,5,6,7-heptamethylindenyl; An = U, X = Cl, L = 1-ethylindenyl). The reaction of U(Ind)Br_3(THF)$_2$ with methyl cyanide containing dry oxygen resulted in ([U(Ind)Br(CH_3CN)$_4$]$_2$O)[UBr_6]. The crystal structure of this compound (Figure 99) revealed a pseudo-pentagonal bipyramidal geometry with the axial oxide bridging two metal centers and with the indenyl ligands in the terminal axial positions. *The U-C8,C9 distances are significantly longer that the U-C1,C2,C3 contacts indicating a more trihapto bonding arrangement. The differences in* bond distances are greater than 0.14Å.

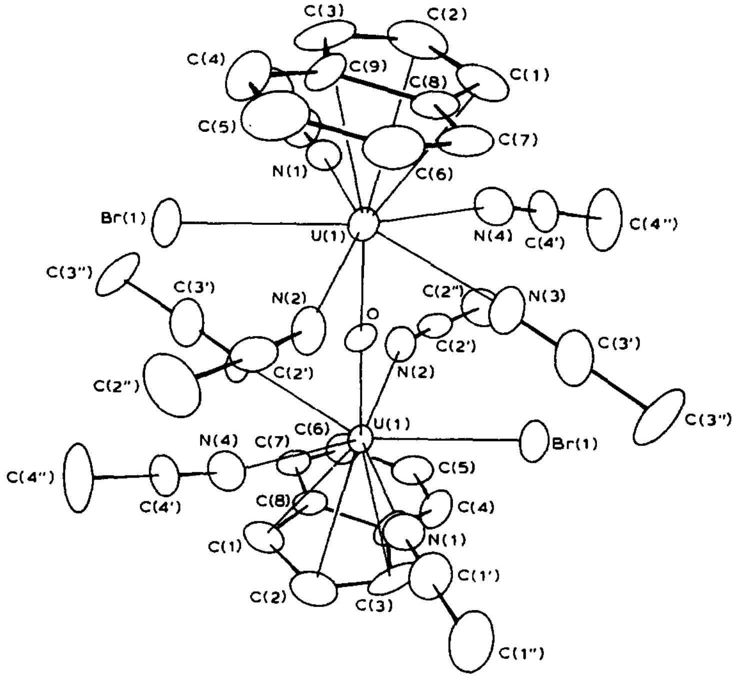

Fig. 99. [(U(Ind)Br(CH_3CN)$_4$)$_2$O]$^{2+}$ cation. (Reprinted with permission from Journal of Organometallic Chemistry.)

Cyclooctatetraenyl, Indenyl, Alkyl Actinide Compounds

(i) Cyclooctatetraenyl ligands. Sevast'yanov and Mitin published the synthesis of 1,1'-di-n-butyluronocene[292] and a study of its volatilization.[293] The compound was prepared by the exchange reaction of U^{3+} and U^{4+} iodides with $Li_2(C_8H_7{}^nC_4H_9)$. Yan, et al. prepared uranocene and studied its volatility.[294]

Wang, Streitwieser and coworkers published three accounts of the preparation and ^1H NMR spectra of 1-1'-dimesityluranocene,[295] 1,1'-di-o-tolyluranocene[295], the corresponding thoracenes,[296] 1,1'-di-t-butylthoracene,[296] and biuranocene.[297] An NMR study of the last one revealed the two uranocene groups to be twisted relative to one another.

Zalkin, et al.[298] reported the disordered crystal structure of dibenzouranocene (Figure 100). The average U-C(π) length is 2.65(7)Å.

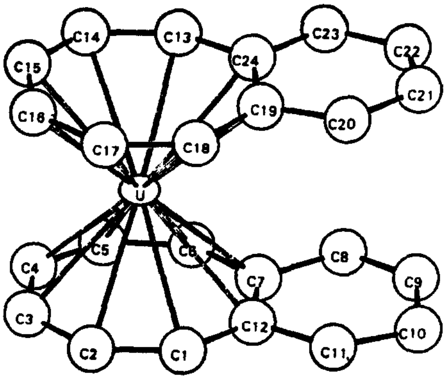

Fig. 100. $[U(C_{12}H_{10})_2]$. (Reprinted with permission from Acta Crystallography.)

Streitwieser, et al.[299] determined the phenyl rotation barrier in 1,1'-diphenyluranocene by variable temperature ^1H NMR. Activation parameters of $\Delta H^{\ddagger} = 4.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -4.7$ eu were observed.

Babcock, et al.[300] reported a flowing afterglow study of uranocene. Ionization fragmentation by He^+ produced $U(C_8H_8)^+$ and $U(C_6H_6)^+$ as the most intense ions. The only uranium containing ion with $N^+/N_2{}^+$ were $U(C_8H_8)_2{}^+$ and $U(C_8H_8)^+$.

Non-relativistic and quasi relativistic SCF-Xα scattered wave calculations on uranocene and thoracene were carried out by Rösch.[190] The f-orbital expansion found in non-relativistic calculations was interpreted to be a consequence of the Xα approximation.

Beach, et al.[301] reported the gas-phase X-ray photoelectron spectra of uranocene. The metal-ring covalency of uranocene was compared to UF_6, $U(BH_4)_4$, and $U(BH_3CH_3)_4$.

1,1'-di-t-butyluranocene was utilized by Todres, et al.[302] in the preparation of azobenzene from nitrobenzene. The reaction was assumed to proceed via formation of a charge transfer complex.

(ii) Arenes. Cotton and coworkers published three reports on uranium arene chemistry. The synthesis, structures, and solid state ^{13}C NMR investigations of $[U(C_6Me_6)Cl_2(\mu\text{-}Cl)_3UCl_2(C_6Me_6)][AlCl_4]$[303,304] (Figure 101) and $U(C_6Me_6)Cl_2(\mu\text{-}Cl)_3UCl_2(\mu\text{-}Cl)_3UCl_2(C_6Me_6)$[303,304] (Figure 102) revealed face sharing pseudo-octahedral U geometries. The average of the U-C(η^6) separations is 2.93(3)Å. The latter compound has a bent chain structure. A trimeric compound, $[U_3(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_3(\mu_1,\eta_2\text{-}AlCl_4)_3(\eta_6\text{-}C_6Me_6)_3][AlCl_4]$[305] was also reported. The crystal structure is shown in Figure 103. The average U-C separation is 2.92Å.

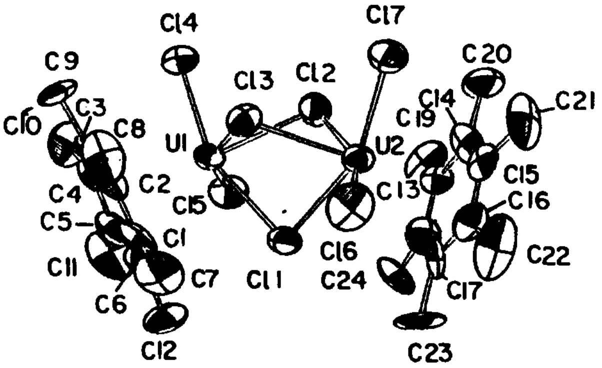

Fig. 101. $[U(C_6Me_6)Cl_2(\mu\text{-}Cl)_3UCl_2(C_6Me_6)]^+$ cation. (Reprinted with permission from Organometallics. Copyright 1986 American Chemical Society.)

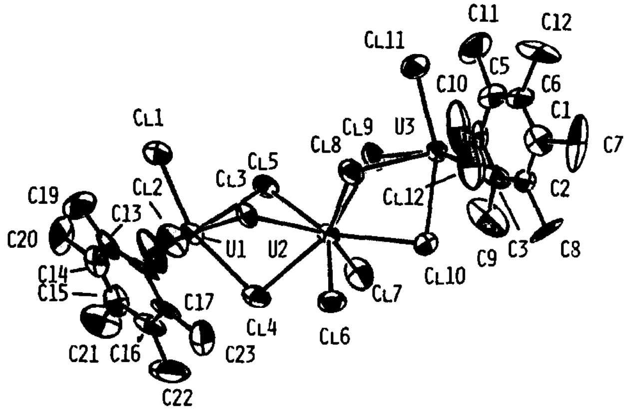

Fig. 102. $[U(C_6Me_6)Cl_2(\mu\text{-}Cl)_3UCl_2(\mu\text{-}Cl)_3UCl_2(C_6Me_6)]$. (Reprinted with permission from Organometallics. Copyright 1986 American Chemical Society.)

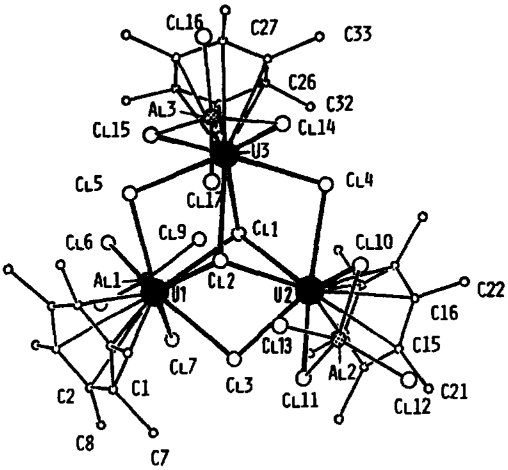

Fig. 103. $[U_3(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_3(\mu_1,\eta^2\text{-}AlCl_4)_3(\eta^6\text{-}C_6Me_6)_3][AlCl_4]$. (Reprinted with permission from Angewandte Chemie International.)

(iii) Akyls, allyls. Marks, et al.[306] prepared the first homoleptic actinide alkyl complex, $[Li(tmeda)]_3ThMe_7\cdot tmeda$ in 1984. The reaction of $ThCl_4$ with LiMe and four equivalents of tmeda in diethyl ether at -78°C produced the yellow compound. The crystal structure is presented in Figure 104. The Th-Me distances range from 2.571(9)Å (C(7)) to 2.765(9)Å (C(4)).

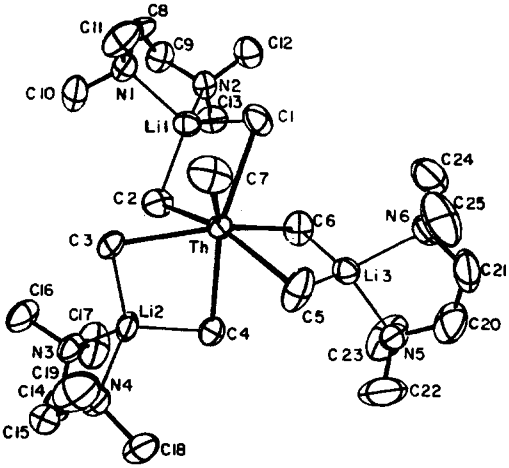

Fig. 104. $[Li(tmeda)]_3ThMe_7 \cdot tmeda$. (Reprinted with permission from Journal of the American Chemical Society. Copyright 1984 American Chemical Society.)

Andersen, Zalkin and Edwards[307] prepared $An(CH_2Ph)_4(dmpe)$ and $An(CH_2Ph)_3Me(dmpe)$ (An = Th, U) by reaction of $AnCl_4(dmpe)$ with lithium alkyls. The crystal structures of $Th(CH_2Ph)_4(dmpe)$ (Figure 105) and $U(CH_2Ph)_3Me(dmpe)$ (Figure 106) were also reported. The actinide alkyl distances observed were $Th-CH_2Ph = 2.55(2)$Å, $U-Me = 2.41(1)$Å, and $U-CH_2Ph = 2.50(4)$Å.

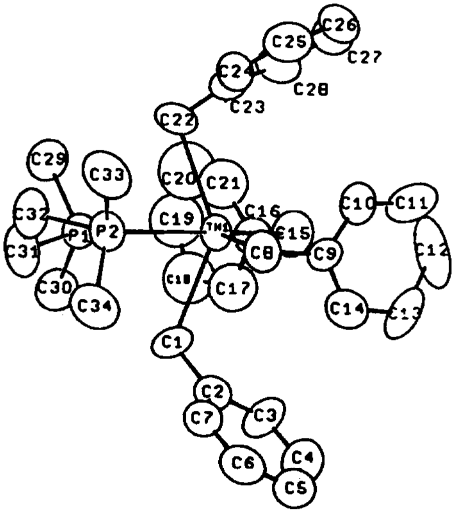

Fig. 105. $Th(CH_2Ph)_4(dmpe)$. (Reprinted with permission from Organometallics. Copyright 1984 American Chemical Society.)

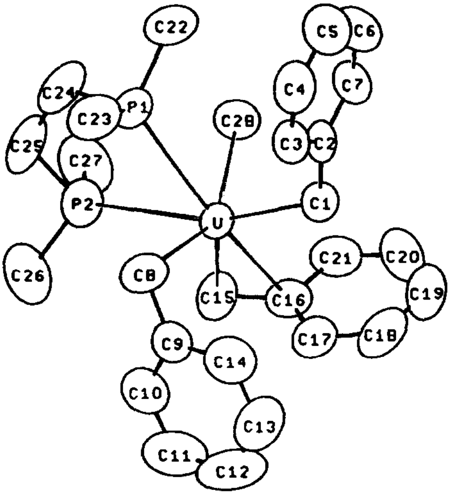

Fig. 106. $U(CH_2Ph)_3Me(dmpe)$. (Reprinted with permission from Organometallics. Copyright 1984 American Chemical Society.)

Seyam[308] published a study of the reaction of UCl_4 and UO_2Cl_2 with lithium alkyls. The decomposition pathways were discussed.

Dormond and coworkers published four accounts of the reactivity of the An-C bond in $An[N(SiMe_3)_2]_2[CH_2SiMe_2NSiMe_3]$.[309-312] The metalocycles were obtained by γ-elimination of methane or hydrogen from $AnMe[N(SiMe_3)_2]_3$ or $AnH[N(SiMe_3)_2]_3$.[309] Carbonyl compounds inserted to give six-membered metalocycles.[309,311] Reactions with the acidic hydrogens of alcohols, phenols and aklynes with pyridine gave the orthometalated products of sp^2 C-H activation; with metal hydrides gave binuclear compounds with isocarbonyl linkages. Cyclopentadienyl compounds cleaved the metal-N bond to give bis-cyclopentadienyl four-membered metalocycles.[310,312]

Toropov, et al.[313,314] published two reports detailing the insertion of CO_2 into the U-allyl bond. Reactions of CO_2 with UR_4, $UR_4OP(OBu)_3$, $UR_4OP(NMe_2)_3$, Cp_3UR, and $Cp_3U(3\text{-}PhR)$ (R = allyl) were studied.

(iv) Packing models. Xing-Fu published three reports on his packing saturation rule for actinides.[198,201,202] These were discussed with the lanthanides.

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